LOWER BOUNDS TO EIGENVALUES OF THE SCHRÖDINGER EQUATION

By

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CHAPTER I

INTRODUCTION

One of the basic problems in quantum theory is the solution of the time-independent Schrödinger equation

$$\mathcal{H}\Psi = E\Psi \tag{1.1}$$

where the Hamiltonian $\mathcal{H}$ is bounded below and has associated with it a set of solutions $\{E_i\}$ corresponding to the discrete levels lying below the continuum.

This equation cannot be solved exactly except for a few cases corresponding to very simple systems. Instead the problem is solved by adopting a suitable method for obtaining an approximate solution. One particularly useful method for treating this problem is the partitioning technique.[1-6] This approach has the interesting feature that it contains many of the more conventional methods such as the variational principle and perturbation theory as special cases.[6]

Using the partitioning technique one may construct a function $\mathcal{E}_1 = f(\epsilon)$, where ϵ is a real variable, having real solutions ϵ_{11}, $\epsilon_{12}, \epsilon_{13}, \ldots, \epsilon_{1g}$ with the property that each pair $(\epsilon, \epsilon_{1i})$ will bracket at least one eigenvalue E of the Hamiltonian $\mathcal{H}$. This means that if ϵ is chosen as an upper bound to an eigenvalue E, at least one of the solutions ϵ_{1i} will be a lower bound to E. The problem of constructing this function and a way of determining which of the

solutions $\mathcal{E}_{1i}$ is the lower bound to E will be studied. The lower bound to E is taken to be the largest of the solutions ϵ_{1i}, (i=1,2, ...,k,k $\leq$ g), providing a lower bound to E. Furthermore, it will be shown that lower bounds to the solutions of $\mathcal{E}_1$ may be constructed by making an inner projection of the reaction operator t_ε with respect to a finite basis, where the reaction operator is associated with the separation of the Hamiltonian $\mathcal{H} = \mathcal{H}_o + V$. Several types of inner projections are discussed with particular emphasis on the "Löwdin Projection."[5]

An application of the method is made to a calculation of lower bounds to some of the ^3S states of He and Li^+ using the "Löwdin Projection."

CHAPTER II

THE PARTITIONING TECHNIQUE AND THE BRACKETING THEOREM

Consider the problem of solving the Schrödinger equation $\mathcal{H}\psi = E\psi$, where the Hamiltonian $\mathcal{H}$ is assumed to be hermitian, i.e., $\mathcal{H}^{+} = \mathcal{H}$ and bounded below. Let $\mathcal{P} = \{\varphi_i\}$ be a complete orthonormal set of functions. As an immediate consequence there is a resolution of the identity,

$$1 = \sum_i |\varphi_i\rangle\langle\varphi_i| \,, \tag{2.1}$$

where the sum over the index i implies summation over the discrete indices and integration over the continuous ones.

Let us define a self-adjoint projection operator $\mathcal{O}$ such that it projects out of the space spanned by $\mathcal{P}$ a subspace $\mathcal{P}_a$ of order g:

$$\mathcal{O} \equiv \sum_{i=1}^{g} |\varphi_i\rangle\langle\varphi_i| \,. \tag{2.2}$$

From this definition it follows that $\mathcal{O}$ satisfies the relations

$$\mathcal{O}^{+} = \mathcal{O} \,, \quad \mathcal{O}^{2} = \mathcal{O} \,, \quad Tr(\mathcal{O}) = g \,. \tag{2.3}$$

Let $P \equiv 1 - \mathcal{O}$ be a projection operator associated with the subspace $\mathcal{P}_b$, the orthogonal complement to the subspace $\mathcal{P}_a$:

$$\mathcal{P}_b = \mathcal{P} - \mathcal{P}_a \,.$$

It then follows that

$$P^2 = P \quad , \quad \mathcal{O}^2 = \mathcal{O} \quad , \quad \mathcal{O}P = P\mathcal{O} = 0. \tag{2.4}$$

The function ψ can be projected onto the complete set $\mathcal{P}$

$$\psi = (\mathcal{O} + P)\,\psi = \mathcal{O}\psi + P\psi \tag{2.5}$$

and the Schrödinger equation can be rewritten as

$$\begin{aligned} \mathcal{H}\psi &= (\mathcal{O}+P)\,\mathcal{H}\,(\mathcal{O}+P)\,\psi \\ &= [\mathcal{O}\mathcal{H}\mathcal{O} + P\mathcal{H}\mathcal{O}]\,\mathcal{O}\psi + [P\mathcal{H}P + \mathcal{O}\mathcal{H}P]\,P\psi \\ &= E\,(\mathcal{O}\psi + P\psi). \end{aligned} \tag{2.6}$$

Operating from the left first by $\mathcal{O}$, then by P, we obtain the set of equations

$$(\mathcal{O}\mathcal{H}\mathcal{O} + \mathcal{O}\mathcal{H}P)\,\psi = E\,\mathcal{O}\psi, \tag{2.7a}$$

$$(P\mathcal{H}\mathcal{O} + P\mathcal{H}P)\,\psi = E\,P\psi. \tag{2.7b}$$

From (2.7b) we find that

$$\begin{aligned} (P\mathcal{H}\mathcal{O})\,\psi &= (P\mathcal{H}\mathcal{O})\,\mathcal{O}\psi = (EP - P\mathcal{H}P)\,\psi \\ &= [P(E-\mathcal{H})P]\,P\psi. \end{aligned} \tag{2.8}$$

From (2.4) we see that, for an arbitrary number α,

$$(\alpha\mathcal{O})P = \alpha(\mathcal{O}P) = \alpha(P\mathcal{O}) = P(\alpha\mathcal{O}) = 0.$$

Then (2.8) can be rewritten in the more general form

$$(P\mathcal{H}\mathcal{O})\,\mathcal{O}\psi = [\alpha\cdot\mathcal{O} + P(E-\mathcal{H})P]\,P\psi. \tag{2.9}$$

Solving (2.9) for $P\psi$, we obtain the expression

$$P\psi = [\alpha\cdot\mathcal{O} + P(E-\mathcal{H})P]^{-1}(P\mathcal{H}\mathcal{O})\otimes\psi. \tag{2.10}$$

Operating on (2.10) from the left by P gives

$$P\psi = \{P[\alpha\cdot\mathcal{O} + P(E-\mathcal{H})P]^{-1}P\mathcal{H}\mathcal{O}\}\otimes\psi. \tag{2.11}$$

Substituting (2.11) for $P\psi$ in equation (2.7a), we obtain

$$\begin{aligned}(\mathcal{O}\mathcal{H}\mathcal{O})\otimes\psi + (\mathcal{O}\mathcal{H}P)P\psi &= E\,\mathcal{O}\psi \\ &= \{\mathcal{O}\mathcal{H}\mathcal{O} + (\mathcal{O}\mathcal{H}P)P[\alpha\cdot\mathcal{O} + P(E-\mathcal{H})P]^{-1}P\mathcal{H}\mathcal{O}\}\otimes\psi \\ &= \{\mathcal{O}[\mathcal{H} + \mathcal{H}P[\alpha\cdot\mathcal{O} + P(E-\mathcal{H})P]^{-1}P\mathcal{H}]\mathcal{O}\}\otimes\psi.\end{aligned} \tag{2.12}$$

Let us introduce the reduced resolvent T_E:[6]

$$T_E \equiv P[\alpha\cdot\mathcal{O} + P(E-\mathcal{H})P]^{-1}P\,. \tag{2.13}$$

Equation (2.12) then becomes

$$[\mathcal{O}(\mathcal{H} + \mathcal{H}T_E\mathcal{H})\mathcal{O}]\otimes\psi = E\,\mathcal{O}\psi. \tag{2.14}$$

Introducing (2.11) and (2.13) into (2.5) we obtain the expression

$$\psi = (1 + T_E\mathcal{H})\otimes\psi. \tag{2.15}$$

Let us introduce the symbolic notation $T_E = \frac{P}{E-\mathcal{H}}$. It is easily seen that T_E satisfies the relations $P(E-\mathcal{H})T_E = P$,

$$\mathcal{O}T_E = T_E\mathcal{O} = 0, \quad PT_E = T_EP = T_E. \tag{2.16}$$

Since $\mathcal{O}\psi = \sum_{i=1}^{g} |\varphi_i\rangle\langle\varphi_i|\psi\rangle = \sum_{i=1}^{g} C_i \varphi_i$, multiplying (2.14) from the left by each of the $\varphi_k \in \mathcal{P}_a$, (k=1,2,...,g) and integrating we obtain a set of g simultaneous equations

$$\sum_{i=1}^{g} \langle \varphi_k | \mathcal{H} + \mathcal{H} T_E \mathcal{H} | \varphi_i \rangle C_i = E C_k , \qquad (k=1,2,\ldots,g). \tag{2.17}$$

This set of equations can be rewritten as a matrix equation

$$\bar{\mathcal{O}}_{aa}(E) \mathbb{C}_a = E \cdot \mathbb{1}_{aa} \mathbb{C}_a , \tag{2.18}$$

where

$$\bar{\mathcal{O}}_{aa}(E) \equiv \langle \mathcal{P}_a | \mathcal{H} + \mathcal{H} T_E \mathcal{H} | \mathcal{P}_a \rangle \tag{2.19}$$

and $\mathbb{C}_a$ is a column vector composed of the coefficients appearing in the expansion of $\mathcal{O}\psi$ in terms of the functions $\varphi_i \in \mathcal{P}_a$.

The solutions to this set of equations are found by setting the determinant of the coefficients of $\mathbb{C}_a$ in the matrix equation $(\bar{\mathcal{O}}_{aa}(E) - E\mathbb{1}_{aa})\mathbb{C}_a = 0$ equal to zero:

$$|\bar{\mathcal{O}}_{aa}(E) - E\mathbb{1}_{aa}| = 0. \tag{2.20}$$

The solutions of the secular equation (2.20) are eigenvalues of $\mathcal{H}$ associated with states not orthogonal to the subspace $\mathcal{P}_a$. This point will be discussed in greater detail later.

One way of solving equation (2.20) is by means of some iterative procedure.[1] Let ε and ε_1 be real variables. By replacing the variable E in $\bar{\mathcal{O}}_{aa}$ with ε, the elements of the matrix $\bar{\mathcal{O}}_{aa}$ become functions of ε and the secular equation (2.20) has a set of g solutions $\{\varepsilon_{1i}\}$ for each value of ε, corresponding to those values of

the variable ε_1 that satisfy the equation

$$\left| \overline{H}_{aa}(\varepsilon) - \varepsilon_1 \mathbb{1}_{aa} \right| = 0 . \tag{2.21}$$

Hence, the variable ε_1 is a multivalued function of ε having the same multiplicity as the order of the subspace $\mathcal{P}_a$ and this is denoted by the expression $\varepsilon_1 = f(\varepsilon)$.

Corresponding to the set of g solutions $\{\varepsilon_{1i}\}$ obtained by solving (2.21) for a fixed value of ε, there will be a set of g vectors $\{a_{a_i}\}$.

Making the substitution of ε for E in (2.19) we obtain the expression

$$\begin{aligned} \overline{H}_{aa}(\varepsilon) &= \langle \mathcal{P}_a | \mathcal{H} + \mathcal{H} T_\varepsilon \mathcal{H} | \mathcal{P}_a \rangle \\ &= \langle \mathcal{P}_a | \mathcal{H} | \mathcal{P}_a \rangle + \langle \mathcal{P}_a | \mathcal{H} | \mathcal{P}_b \rangle \langle \mathcal{P}_b | T_\varepsilon | \mathcal{P}_k \rangle \\ &\quad \times \langle \mathcal{P}_b | \mathcal{H} | \mathcal{P}_a \rangle \\ &= H_{aa} + H_{ab} T_{bb}(\varepsilon) H_{ba} \end{aligned} \tag{2.22}$$

where

$$\begin{aligned} H_{ij} &\equiv \langle \mathcal{P}_i | \mathcal{H} | \mathcal{P}_j \rangle , \\ T_{bb}(\varepsilon) &\equiv \langle \mathcal{P}_b | T_\varepsilon | \mathcal{P}_b \rangle . \end{aligned} \tag{2.23}$$

Then, for arbitrary ε, each of the solutions ε_{1i} (i=1,2,...,g) may be expressed as a function of ε, i.e., $\varepsilon_{1i} = f_i(\varepsilon)$, having the form:

$$\mathcal{E}_{ii} = \frac{\mathbb{C}_{ai}^{+}\, \overline{\mathbb{H}}_{aa}(\mathcal{E})\, \mathbb{C}_{ai}}{\mathbb{C}_{ai}^{+}\, \mathbb{C}_{ai}} = f_i(\mathcal{E}) \,. \tag{2.24}$$

Taking the first derivative of (2.24) with respect to $\mathcal{E}$ and evaluating it at the same value of $\mathcal{E}$ for which the $\mathbb{C}_{ai}$ were evaluated, we have[7]

$$\frac{d\mathcal{E}_{ii}}{d\mathcal{E}} = \frac{\mathbb{C}_{ai}^{+}\, \frac{d\,\overline{\mathbb{H}}_{aa}(\mathcal{E})}{d\mathcal{E}}\, \mathbb{C}_{ai}}{\mathbb{C}_{ai}^{+}\, \mathbb{C}_{ai}}$$

$$= \frac{\mathbb{C}_{ai}^{+}\, \mathbb{H}_{ab}\, \frac{d\,\mathbb{T}_{bb}(\mathcal{E})}{d\mathcal{E}}\, \mathbb{H}_{ba}\, \mathbb{C}_{ai}}{\mathbb{C}_{ai}^{+}\, \mathbb{C}_{ai}} \,. \tag{2.25}$$

We see from (2.23) that

$$\frac{d\,\mathbb{T}_{bb}(\mathcal{E})}{d\mathcal{E}} = \langle \mathbb{P}_b | \frac{d}{d\mathcal{E}} \left(\frac{P}{\mathcal{E}-\mathcal{H}} \right) | \mathbb{P}_b \rangle = -\langle \mathbb{P}_b | \mathbb{T}_{\mathcal{E}}^{2} | \mathbb{P}_b \rangle . \tag{2.26}$$

We then see from (2.16) and (2.23) that

$$-\langle \mathbb{P}_b | \mathbb{T}_{\mathcal{E}}^{2} | \mathbb{P}_b \rangle = -\langle \mathbb{P}_b | \mathbb{T}_{\mathcal{E}} | \mathbb{P}_b \rangle \langle \mathbb{P}_b | \mathbb{T}_{\mathcal{E}} | \mathbb{P}_b \rangle$$

$$= -\,\mathbb{T}_{bb}^{2}(\mathcal{E}) \,,$$

from which it follows that

$$\frac{d\,\mathbb{T}_{bb}(\mathcal{E})}{d\mathcal{E}} = -\,\mathbb{T}_{bb}^{2}(\mathcal{E}) < 0 \,. \tag{2.27}$$

Replacing $\frac{d\mathcal{T}_{bb}(\mathcal{E})}{d\mathcal{E}}$ in (2.25) by the right hand side of (2.27), we obtain the result

$$\frac{d\mathcal{E}_{1i}}{d\mathcal{E}} = - \frac{\mathcal{C}_{ai}^{+} \mathcal{H}_{aq} \mathcal{T}_{bb}^{2}(\mathcal{E}) \mathcal{H}_{ba} \mathcal{C}_{ai}}{\mathcal{C}_{ai}^{+} \mathcal{C}_{ai}}$$

$$= - \frac{(\mathcal{H}_{bq} \mathcal{C}_{ai})^{+} \mathcal{T}_{bb}^{2}(\mathcal{E}) (\mathcal{H}_{ba} \mathcal{C}_{ai})}{\mathcal{C}_{ai}^{+} \mathcal{C}_{ai}} \qquad (2.28)$$

$$< 0 , \qquad (i=1,2,\ldots,g)$$

Therefore, each of the solutions $\mathcal{E}_{1i}$ is a function of $\mathcal{E}$ having a negative slope for all $\mathcal{E}$.

Let $\mathcal{E} = E + \epsilon$, where ϵ is the difference between the value of $\mathcal{E}$ and some eigenvalue E of $\mathcal{H}$. Let one of the solutions given by (2.24) be represented as $\mathcal{E}_{1i} = E + \epsilon_{1i}$. If ϵ is a small quantity, we can use the Lagrange mean-value theorem to obtain the result that

$$\mathcal{E}_{1i} = E + \epsilon_{1i} = f_i(\mathcal{E}) = f_i(E + \theta\epsilon)$$

$$= f_i(E) + \epsilon f_i'(E + \theta\epsilon) ,$$

where $0 \leq \theta \leq 1$. Using the identity $E = f_i(E)$ (see (2.18)) we obtain the relation

$$\epsilon_{1i} = \epsilon f_i'(E + \theta\epsilon) . \qquad (2.29)$$

From (2.28) we know that the first derivative f_i' is negative; hence,

the quantities ϵ and ϵ_{1i} have different signs. This leads to the bracketing theorem[1] which says that the pair $(\epsilon, \epsilon_{1i})$ bracket at least one true eigenvalue of $\mathcal{H}$. Then the g intervals $(\epsilon, \epsilon_{1i})$ will each contain at least one true eigenvalue E such that if $\epsilon < E$, then $\epsilon_{1i} > E$ and vice versa.

Let us examine the behavior of $\overline{\mathcal{D}}_{aa}(\mathcal{E})$ in the limit of $\mathcal{E} \to \pm\infty$. We see from (2.22) that

$$\lim_{\mathcal{E}\to\pm\infty} \overline{\mathcal{D}}_{aa}(\mathcal{E}) = \lim_{\mathcal{E}\to\pm\infty} \left(\mathcal{D}_{aa} + \mathcal{D}_{ab} \pi_{bb}(\mathcal{E}) \mathcal{D}_{ba} \right)$$

$$= \mathcal{D}_{aa} + \mathcal{D}_{ab} \left\{ \lim_{\mathcal{E}\to\pm\infty} \langle \mathcal{P}_b | \frac{P}{\mathcal{E} - \mathcal{H}} | \mathcal{P}_b \rangle \right\} \mathcal{D}_{ba} \qquad (2.30)$$

$$= \mathcal{D}_{aa} .$$

Hence, the set of g solutions $\{\mathcal{E}_{1i}\}$ have as horizontal asymptotes the eigenvalues of the matrix $\mathcal{D}_{aa}$:

$$\lim_{\mathcal{E}\to\pm\infty} \mathcal{E}_{1i} = \lim_{\mathcal{E}\to\pm\infty} \frac{\mathcal{C}_{ai}^{+} \overline{\mathcal{D}}_{aa}(\mathcal{E}) \mathcal{C}_{ai}}{\mathcal{C}_{ai}^{+} \mathcal{C}_{ai}}$$

$$= \frac{\mathcal{C}_{ai}^{+} \mathcal{D}_{aa} \mathcal{C}_{ai}}{\mathcal{C}_{ai}^{+} \mathcal{C}_{ai}} = h_i \quad . \qquad (2.31)$$

Let us define the "outer projection" $\overline{\mathcal{H}}$ by the relation

$$\overline{\mathcal{H}} = P \mathcal{H} P .$$

Since $P\mathcal{O} = \mathcal{O}P = 0$, it follows that all the functions $\mathcal{P}_i \in \mathcal{P}_a$ are eigenfunctions of $\overline{\mathcal{H}}$ associated with the eigenvalue 0.

Let us consider the normalized eigenfunctions $\bar{\psi}_i$ of $\bar{\mathcal{H}}$ associated with the eigenvalues $\bar{E}_i$ that are situated in the subspace $\mathcal{P}_b$. We then have the spectral resolutions[3]

$$P = \sum_i |\bar{\psi}_i\rangle\langle\bar{\psi}_i| \,, \qquad \bar{\mathcal{H}} = \sum_i \bar{E}_i |\bar{\psi}_i\rangle\langle\bar{\psi}_i| \,, \quad T_\varepsilon = \sum_i \frac{|\bar{\psi}_i\rangle\langle\bar{\psi}_i|}{\varepsilon - \bar{E}_i} \,. \tag{2.32}$$

It is obvious that the reaction operator has <u>vertical asymptotes</u> for the values $\varepsilon = \bar{E}_i$, $(i=1,2,\ldots)$. It then follows that the bracketing function ε_1 has vertical asymptotes for the values $\varepsilon = \bar{E}_i$, provided $\bar{E}_i$ is not simultaneously an eigenvalue of $\mathcal{H}$.

Let ψ_i be a function satisfying the Schrödinger equation $\mathcal{H}\psi_i = E_i\psi_i$. From (2.5), we see that $\psi_i = Q\psi_i + P\psi_i$. Therefore, if $Q\psi_i = 0$ and $P\psi_i \neq 0$, it follows that

$$\psi_i = P\psi_i = \bar{\psi}_i \,. \tag{2.33}$$

Then, from (2.7a) and (2.7b) we find that

$$(Q\mathcal{H}P)\bar{\psi}_i = Q\mathcal{H}\psi_i = E_i Q\psi_i = 0 \,, \qquad \bar{\mathcal{H}}\bar{\psi}_i = (P\mathcal{H}P)\bar{\psi}_i = E_i\bar{\psi}_i \,. \tag{2.34}$$

That is, for those values $\varepsilon = E_i$ where E_i is an eigenvalue of $\mathcal{H}$ associated with a state ψ_i that is orthogonal to the reference manifold $\mathcal{P}_a$, ψ_i is also an eigenstate of $\bar{\mathcal{H}}$ having the same eigenvalue, i.e., $\bar{E}_i = E_i$.

Let us make the separation

$$P = P' + P'' \,, \tag{2.35}$$

where $P' \equiv \sum_{\alpha} |\psi_\alpha\rangle\langle\psi_\alpha|$ for all the $\psi_\alpha = \bar{\psi}_\alpha$ such that $\mathcal{O}\psi_\alpha = 0$ and

$P'' \equiv \sum_{\beta} |\bar{\psi}_\beta\rangle\langle\bar{\psi}_\beta|$ for all the $\bar{\psi}_\beta$ such that $\mathcal{O}\bar{\psi}_\beta \neq 0$.

The reaction operator T_ε may then be separated:

$$T_\varepsilon = \sum_{\alpha} \frac{|\psi_\alpha\rangle\langle\psi_\alpha|}{\varepsilon - E_\alpha} + \sum_{\beta} \frac{|\bar{\psi}_\beta\rangle\langle\bar{\psi}_\beta|}{\varepsilon - \bar{E}_\beta} \qquad (2.36)$$

$$= T_\varepsilon' + T_\varepsilon''.$$

It then follows from (2.22) that

$$(\bar{\mathcal{H}}_{aa}(\varepsilon))_{kl} = \bar{H}_{kl}(\varepsilon) = \langle\varphi_k| \mathcal{H} + \mathcal{H}(T_\varepsilon' + T_\varepsilon'')\mathcal{H}|\varphi_l\rangle$$

$$= H_{kl} + \sum_{\alpha} \frac{\langle\varphi_k|\mathcal{H}|\psi_\alpha\rangle\langle\psi_\alpha|\mathcal{H}|\varphi_l\rangle}{\varepsilon - E_\alpha} \qquad (2.37)$$

$$+ \sum_{\beta} \frac{\langle\varphi_k|\mathcal{H}|\bar{\psi}_\beta\rangle\langle\bar{\psi}_\beta|\mathcal{H}|\varphi_l\rangle}{\varepsilon - \bar{E}_\beta}.$$

Since $\mathcal{H}\psi_\alpha = E_\alpha\psi_\alpha$ and $\mathcal{O}\psi_\alpha = 0$, we see that $\langle\varphi_k|\mathcal{H}|\psi_\alpha\rangle = E_\alpha\langle\varphi_k|\psi_\alpha\rangle = 0$ for all $\varphi_k \in \mathcal{P}_a$. Hence the second term in (2.37) drops out and we obtain the final result

$$\bar{H}_{kl}(\varepsilon) = H_{kl} + \sum_{\beta} \frac{H_{k\beta} H_{\beta l}}{\varepsilon - \bar{E}_\beta}, \qquad (2.38)$$

where

$$H_{k\beta} \equiv \langle\varphi_k|\mathcal{H}|\bar{\psi}_\beta\rangle.$$

From (2.38) it is easily seen that for $\varepsilon = E_i$, where E_i is a solution of $\mathcal{H}\psi_i = E\psi_i$ and $\mathcal{O}\psi_i = 0$, the bracketing function ε_1 has no

vertical asymptote. Further, we see that $\mathcal{E}_1$ has vertical asymptotes only for those values of $\mathcal{E}$ corresponding to eigenvalues of $P\mathcal{H}P$ not simultaneously eigenvalues of $\mathcal{H}$, i.e., only for those cases where $\mathcal{O}\bar{\psi}_i \neq 0$.

It follows from the variation principle[8] that the eigenvalues of $\bar{\mathcal{H}}$ are upper bounds to the eigenvalues of $\mathcal{H}$ in order,

$$\bar{E}_k \geq E_k . \tag{2.39}$$

Hence the vertical asymptotes appear in the bracketing function $\mathcal{E}_1$ for values of $\mathcal{E}$ that are upper bounds to eigenvalues of $\mathcal{H}$ corresponding to the states ψ_i satisfying the criterion that $\mathcal{O}\psi_i \neq 0$.

A plot of the g-valued function $\mathcal{E}_1$ as a function of the variable $\mathcal{E}$ can be made by imposing the non-crossing rule, which is valid for states having the same symmetry. The values of the g curves will satisfy the relation

$$\mathcal{E}_{1i} \geq E_i \quad , \qquad (i=1,2,\ldots,g), \tag{2.40}$$

for all $\mathcal{E} < E_1$. If $\mathcal{E}_{11}$ is taken to be the lowest value of the set of solutions $\{\mathcal{E}_{1i}\}$, then for $\mathcal{E}$ chosen equal to E_1 we find that $\mathcal{E}_{11} = E_1$ provided that $\mathcal{O}\psi_1 \neq 0$. Then for $\mathcal{E} > E_1$, we see from (2.29) that $\mathcal{E}_{11} < E_1$ and the $\mathcal{E}_{11}$ curve will undergo a discontinuous change from $-\infty$ to $+\infty$ as $\mathcal{E}$ passes through $\bar{E}_1$. In general, we find that the g curves have the behavior illustrated in Fig. 1, which is for g = 3. We see that each branch of the curves crosses the $\mathcal{E}_1 = \mathcal{E}$ line at an eigenvalue of $\mathcal{H}$ associated with a state ψ_i not orthogonal to the reference manifold $\mathcal{P}_a$.

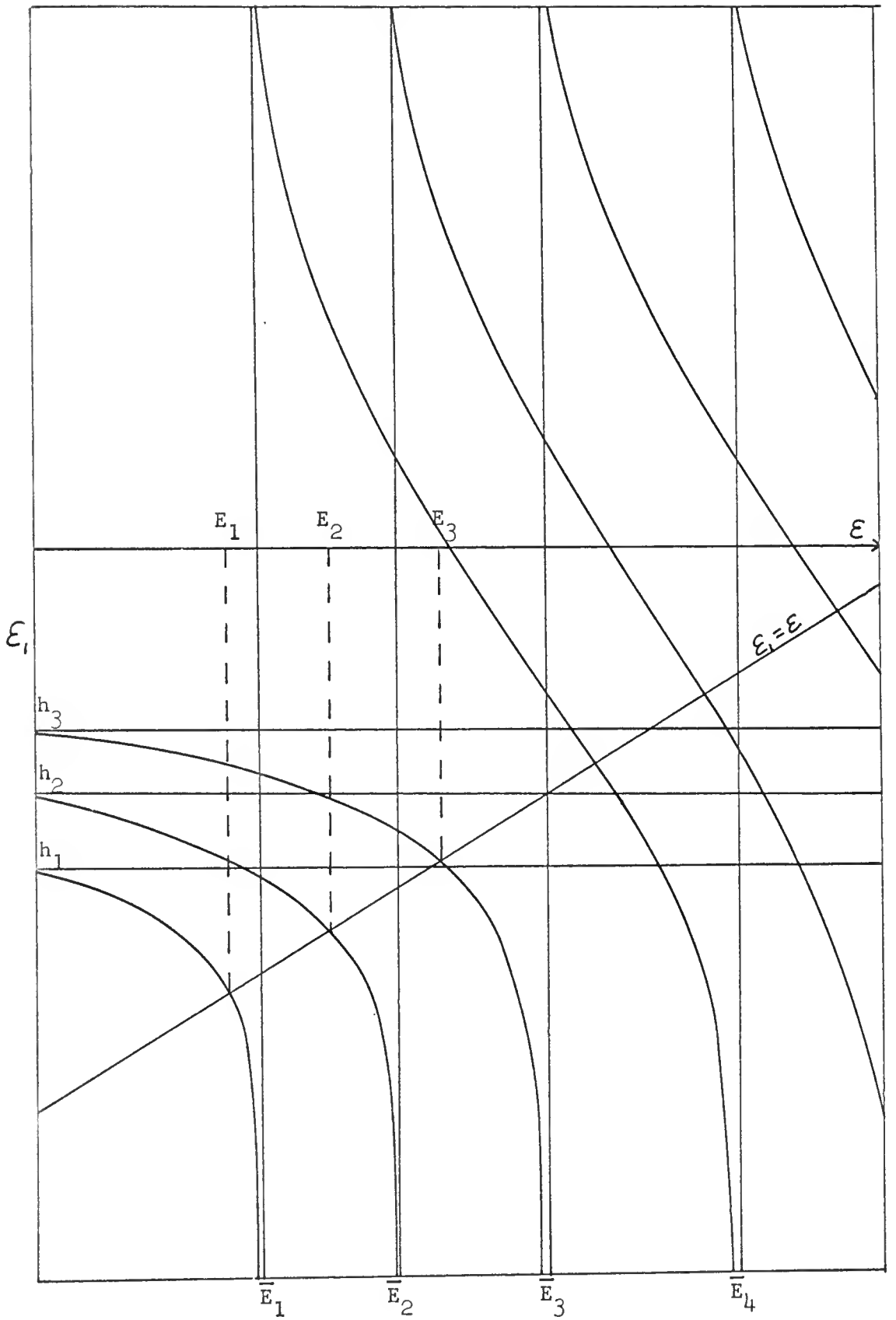

Fig. 1. Typical behavior of the multivalued bracketing function $\varepsilon_1 = f(\varepsilon)$ for g = 3.

It is apparent from this discussion that for $\Theta\psi_i \neq 0$ and $E_i < \varepsilon < \bar{E}_i$, one of the eigenvalues of $\overline{\Theta\Theta}_{aa}(\varepsilon)$, ε_{1k}, is the lower bound to E_i, i.e., E_i lies in the interval $(\varepsilon_{1k}, \varepsilon)$ and for $\varepsilon = E_i$, $\varepsilon_{1k} = E_i$.

CHAPTER III

LOWER BOUNDS TO ENERGY STATES

Assume that the Hamiltonian $\mathcal{H}$ of a system may be separated into two parts; a zeroth order Hamiltonian or unperturbed part $\mathcal{H}_0$ and the interaction part or perturbation V. Let there be associated with the Hamiltonian $\mathcal{H}_0$ a complete orthonormal set of eigenfunctions $\{\varphi_i^0\}$ and a known eigenvalue spectrum E_i^0, (i=1,2,...), such that

$$\mathcal{H}_0 \varphi_i^0 = E_i^0 \varphi_i^0 \ . \tag{3.1}$$

Let it be further assumed that the perturbation V is positive definite:

$$V > 0 \ . \tag{3.2}$$

The space $\mathcal{S}^0$ spanned by the set $\{\varphi_i^0\}$ can be partitioned into two subspaces $\mathcal{S}_a^0$ and $\mathcal{S}_b^0$ by defining the projection operators

$$\mathcal{O} = \sum_{i=1}^{g} |\varphi_i^0\rangle\langle\varphi_i^0| = \sum_{i=1}^{g} \mathcal{O}_i^0 \ , \tag{3.3}$$

$$P = 1 - \mathcal{O} = \sum_{j=g+1} |\varphi_j^0\rangle\langle\varphi_j^0| = \sum_{j=g+1} P_j^0 \ ,$$

such that

$$\mathcal{O}\,\mathcal{S}^0 = \mathcal{S}_a^0 \ , \quad P\,\mathcal{S}^0 = \mathcal{S}_b^0 \ . \tag{3.4}$$

The operators $\mathcal{O}$ and P satisfy the relations given in (2.3) and (2.4). From (3.1) we also see that

$$\mathcal{O}\mathcal{H}_0 = \mathcal{H}_0\mathcal{O} = \sum_{i=1}^{q} E_i^\circ |\varphi_i^\circ\rangle\langle\varphi_i^\circ| ,$$

and using (2.16) we have the result

$$\mathcal{O}\mathcal{H}_0 T_\varepsilon = \mathcal{H}_0 \mathcal{O} T_\varepsilon = 0.$$

Equation (2.19) may be rewritten as

$$\bar{H}_{aa}(\varepsilon) = \langle \Phi_a^\circ | \mathcal{H}_0 + V + V T_\varepsilon V | \Phi_a^\circ \rangle . \tag{3.5}$$

Let us introduce a reduced resolvent T_0 associated with the unperturbed Hamiltonian $\mathcal{H}_0$,

$$T_0 = \frac{P}{\varepsilon - \mathcal{H}_0} = \sum_{j=q+1} \frac{P_j^\circ}{\varepsilon - E_j^\circ} , \tag{3.6}$$

where again the sum implies summation over the discrete states and integration over the continuous part of the spectrum.

For any inverse operator of the type $(A-B)^{-1}$ there are the following identities:

$$\begin{aligned} (A-B)^{-1} &= A^{-1} + A^{-1}B(A-B)^{-1} \\ &= A^{-1} + (A-B)^{-1}BA^{-1} , \end{aligned} \tag{3.7}$$

provided the inverse operators involved actually exist. Using the first of the identities given in (3.7) we find that

$$\begin{aligned} T_\varepsilon &= T_0 + T_0 V T_\varepsilon , \\ T_\varepsilon V &= T_0 (V + V T_\varepsilon V) = T_0 \mathcal{T}_\varepsilon , \end{aligned} \tag{3.8}$$

where $t_\varepsilon \equiv V + V T_\varepsilon V \equiv V + V T_o t_\varepsilon$ (3.9)

is the reaction operator.[2] The last relation corresponds to the Lippmann-Schwinger integral equation in scattering theory.

Provided V^{-1} exists, we find from (3.9) that $(V^{-1}-T_o)t_\varepsilon = 1$; hence,

$$t_\varepsilon = (V^{-1} - T_o)^{-1}. \tag{3.10}$$

Assuming the spectrum of $\mathcal{H}_o$ is ordered, $E_1^o < E_2^o < E_3^o < \ldots$, it is easily seen from (3.6) that for $\varepsilon < E_{g+1}^o$, $T_o < 0$. Since it is assumed that $V > 0$, we see that $V^{-1} > 0$ and hence $t_\varepsilon > 0$.

Introducing (3.9) into equation (3.5) we obtain

$$\overline{\mathcal{H}}_{aa}(\varepsilon) = \langle \mathcal{P}_a^o \mid \mathcal{H}_o + t_\varepsilon \mid \mathcal{P}_a^o \rangle \equiv \mathcal{E}_1 . \tag{3.11}$$

Hence, we see that the choice of $\mathcal{O}$ as given in (3.3) leads to a multi-valued bracketing function $\mathcal{E}_1$. From Chapter II, it follows that this bracketing function will have vertical asymptotes only for those states ψ_k of $\mathcal{H}$ that satisfy the relation $\mathcal{O}\psi_k \neq 0$. That is, only those states not orthogonal to the reference manifold $\mathcal{P}_a^o$, spanned by the set of g eigenvectors of $\mathcal{H}_o$, will cause vertical asymptotes to appear in $\mathcal{E}_1$. The function $\mathcal{E}_1$ has the important property that the first vertical asymptote occurs for $\varepsilon > E_{g+1}^o$. Hence, if $P\mathcal{H}P$ has the ordered spectrum $\bar{E}_1 < \bar{E}_2 < \ldots$, then $\bar{E}_1 > E_{g+1}^o$. To prove this let us consider two self-adjoint operators A and B satisfying the relation

$$A > B. \tag{3.12}$$

Then, for any function φ, $\langle \varphi | A | \varphi \rangle > \langle \varphi | B | \varphi \rangle$.

Let P be an arbitrary linear operator. Then replacing φ by $P\varphi$ we find that $\langle\varphi|P^+AP|\varphi\rangle > \langle\varphi|P^+BP|\varphi\rangle$, i.e.,

$$P^+AP > P^+BP. \tag{3.13}$$

Since $V > 0$ we have the inequality $\mathcal{H} = \mathcal{H}_0 + V > \mathcal{H}_0$, where $\mathcal{H}^+ = \mathcal{H}$ and $\mathcal{H}_0^+ = \mathcal{H}_0$. Then from (3.13) we find that for the self-adjoint projection operator P defined in (3.3)

$$P\mathcal{H}P > P\mathcal{H}_0P. \tag{3.14}$$

Hence, $\langle\varphi|P\mathcal{H}P|\varphi\rangle > \langle\varphi|P\mathcal{H}_0P|\varphi\rangle$ for any function φ. Let $\varphi = \bar{\psi}_1$, where $\bar{\psi}_1$ is the lowest state of $P\mathcal{H}P$ not orthogonal to φ_a^o. Since the ground state of $P\mathcal{H}_0P$ is E^o_{g+1}, it follows from the variation principle[8] that

$$\bar{E}_1 = \langle\bar{\psi}_1|P\mathcal{H}P|\bar{\psi}_1\rangle > \langle\bar{\psi}_1|P\mathcal{H}_0P|\bar{\psi}_1\rangle \geq E^o_{g+1}. \tag{3.15}$$

It follows at once that the first vertical asymptote of $\mathcal{E}_1$ appears for $\mathcal{E} > E^o_{g+1}$. In general, the eigenvalues of a self-adjoint operator A are greater than or equal to the eigenvalues of a self-adjoint operator B in order if $A > B$.[2]

It is an immediate consequence of this that for $\mathcal{E} < E^o_{g+1}$, $t_\mathcal{E}^{-1}$ exists and satisfies the inequality[2,9]

$$t_\mathcal{E}^{-1} = V^{-1} - T_0 \geq V^{-1} > 0. \tag{3.16}$$

Hence $V \geq t_\mathcal{E} > 0$ and $\mathcal{H}_0 + V \geq \mathcal{H}_0 + t_\mathcal{E} > \mathcal{H}_0$. Applying (3.13) we find

$$\mathcal{O}(\mathcal{H}_0+V)\mathcal{O} \geq \mathcal{O}(\mathcal{H}_0+t_\mathcal{E})\mathcal{O} > \mathcal{O}\mathcal{H}_0\mathcal{O}$$

and therefore,

$$h_i \geq \mathcal{E}_{1i} > E_i^o, \qquad (i=1,2,\ldots,g). \qquad (3.17)$$

This says that the eigenvalues of $\mathcal{E}_1$ are bounded above by the average values of $\mathcal{H}$ with respect to the basis Φ_a^o and bounded below by the eigenvalues of $\mathcal{H}_o$ <u>in order</u> for $\mathcal{E} < E_{g+1}^o$.

For each value of $\mathcal{E}$, $\mathcal{E}_1$ will satisfy the equation

$$(\mathcal{E}_1 - \mathcal{E}_{1i}\mathbb{1})\, C_i = 0, \qquad (i=1,2,\ldots,g). \qquad (3.18)$$

From this it follows that for any $\mathcal{E}$ the curves $\mathcal{E}_{1i}$, $(i=1,2,\ldots,g)$, have negative definite slopes. From (3.10) and (3.11) we have

$$\frac{d\mathcal{E}_1}{d\mathcal{E}} = \frac{d}{d\mathcal{E}} \langle \Phi_a^o | \mathcal{H}_o + (V^{-1} - T_o)^{-1} | \Phi_a^o \rangle \qquad (3.19)$$

$$= -\langle \Phi_a^o | (V^{-1} - T_o)^{-1} \left(-\frac{dT_o}{d\mathcal{E}}\right) (V^{-1} - T_o)^{-1} | \Phi_a^o \rangle .$$

We see from (2.26) that $-\frac{dT_o}{d\mathcal{E}} = T_o^2$. Making this substitution in (3.19) we obtain

$$\frac{d\mathcal{E}_1}{d\mathcal{E}} = \langle \Phi_a^o | t_\mathcal{E} (-T_o^2) t_\mathcal{E} | \Phi_a^o \rangle \qquad (3.20)$$

$$= -\langle T_o t_\mathcal{E} \Phi_a^o | T_o t_\mathcal{E} \Phi_a^o \rangle < 0.$$

Each of the curves has a slope at the point $\mathcal{E}$ for which $\mathcal{E}_{1i}$ and C_i were evaluated given by

$$\left.\frac{d\mathcal{E}_{1i}}{d\mathcal{E}'}\right|_{\mathcal{E}'=\mathcal{E}} = C_i^+ \left.\frac{d\mathcal{E}_1}{d\mathcal{E}'} C_i\right|_{\mathcal{E}'=\mathcal{E}} < 0, \qquad (3.21)$$

$$(i=1,2,\ldots,g).$$

Hence, the curves have negative definite slopes and the bracketing theorem[1] holds for each of the g eigenvalues of $\mathcal{E}_1$. From (3.21) and the inequality (3.15) it follows that for every $E_k < \mathcal{E} < E^o_{g+1}$, where E_k is the k th lowest eigenvalue of the Hamiltonian $\mathcal{H}$ associated with a state ψ_k not orthogonal to the subspace $\mathcal{S}^o_a$, there is at least one solution to (3.18) that will provide a lower bound to E_k. In fact, it is now easy to prove that under these conditions the k th lowest solution of (3.18) is the lower bound (or highest lower bound) to E_k.

From the discussion associated with Fig. 1, we observe that the curves of $\mathcal{E}_1$ cross the $\mathcal{E}_1 = \mathcal{E}$ line at the eigenvalues of $\mathcal{H}$ associated with states ψ_i having the property that $\mathcal{O}\psi_i \neq 0$. From (3.15) we found that the first vertical asymptote was situated to the right of E^o_{g+1}, i.e., $\bar{E}_1 > E^o_{g+1}$. Let there be k eigenvalues of $\mathcal{H}$ having the ordering $E_1 < E_2 < \ldots < E_k < E^o_{g+1}$, associated with states satisfying the above property. Let the eigenvalues of $\mathcal{E}_1$ also be ordered, i.e., $\mathcal{E}_{11} < \mathcal{E}_{12} < \cdots < \mathcal{E}_{1g}$. Then, $\mathcal{E}_{11}$ is the lower bound to E_1 for $E_1 < \mathcal{E} < E^o_{g+1}$ and is equal to E_1 for $\mathcal{E} = E_1$. In order to see this let us assume there exists for some $j > 1$ a solution $\mathcal{E}_{1j}$ such that $\mathcal{E}_{1j} = E_1$ for $\mathcal{E} = E_1$. Then, from the non-crossing rule and (3.21), $\mathcal{E}_{11}$ must be $< E_1$ and hence crosses the $\mathcal{E}_1 = \mathcal{E}$ line for some value of $\mathcal{E} < E_1$. This contradicts the assumption that E_1 is the lowest eigenvalue of $\mathcal{H}$ associated with a state ψ satisfying the requirement that $\mathcal{O}\psi \neq 0$. Similarly, $\mathcal{E}_{12}$ provides the lower bound (or highest lower bound) to E_2 for $E_2 < \mathcal{E} < E^o_{g+1}$. If for some $j > 2$ there exists a solution $\mathcal{E}_{1j}$ such that $\mathcal{E}_{1j} = E_2$ for $\mathcal{E} = E_2$, then by once again

imposing the non-crossing rule and (3.21) we find that ε_{12} must cross the $\varepsilon_1 = \varepsilon$ line for a value $E_1 < \varepsilon < E_2$ which leads to a contradiction. By induction, we see that, for any $E_i < \varepsilon < E^o_{g+1}$, ε_{1i} is the lower bound to E_i, $(i=1,2,\ldots,k)$.

Figure 2 illustrates the typical behavior of the multivalued bracketing function (3.11) for g = 4 and k = 2.

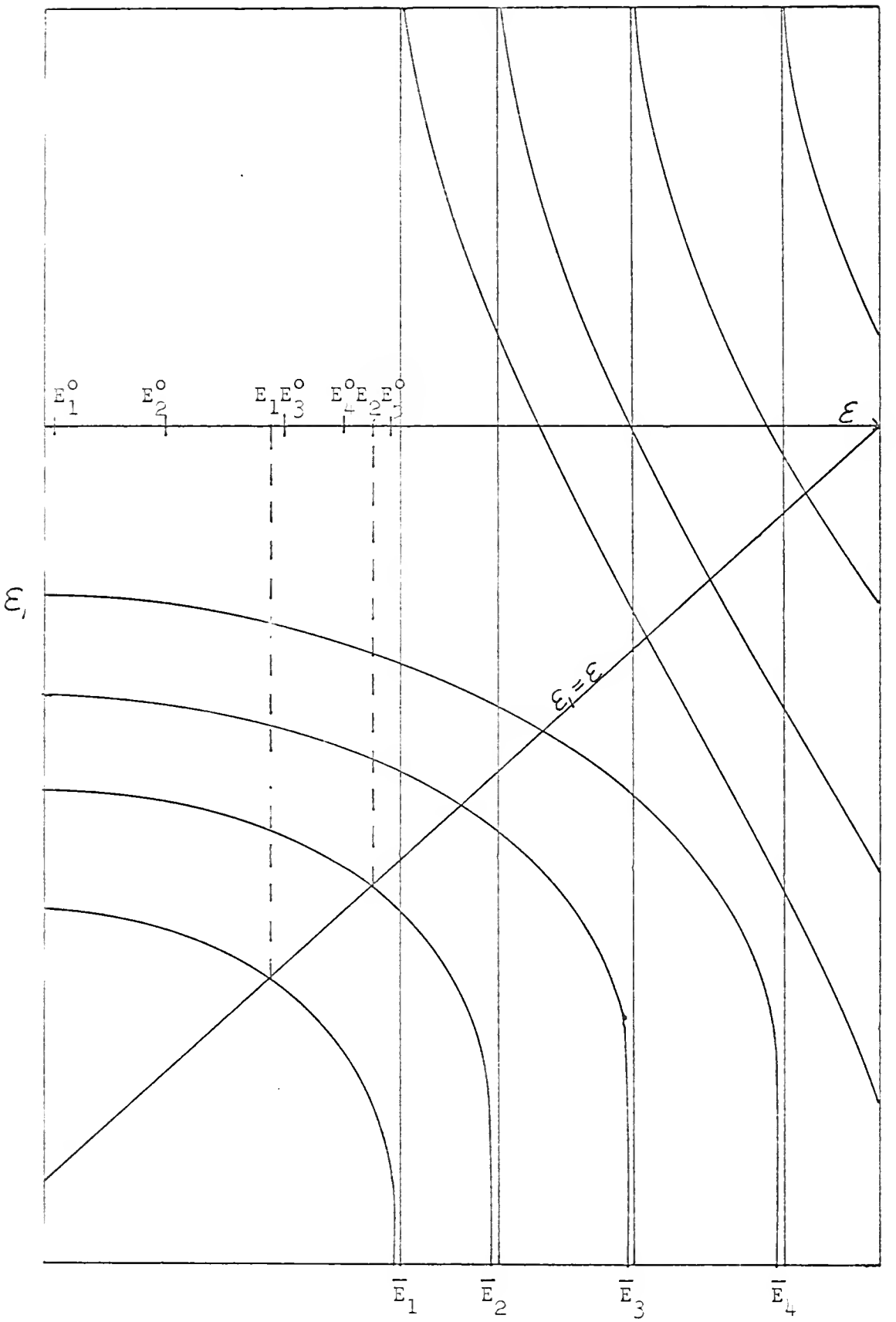

Fig. 2. Typical behavior of the multivalued bracketing function $\mathcal{E}_1$ for g = 4 and k = 2.

CHAPTER IV

LOWER BOUNDS TO THE REACTION OPERATOR

In principle, equation (3.11) can be solved exactly and provides lower bounds to those states of the Hamiltonian $\mathcal{H}$ satisfying the criteria that $\mathcal{O}\psi_i \neq 0$ and $\mathcal{E} < E^o_{g+1}$. In fact, there are few problems for which (3.11) can be solved exactly.

From (3.10) we see that the reduced resolvent T_o must first be obtained in order to calculate the reaction operator $t_\mathcal{E}$. From (3.6) we know that $T_o < 0$ for $\mathcal{E} < E^o_{g+1}$. If T_o cannot be evaluated exactly, one approach would be to estimate it by the operator $T_o(p)$:

$$T_o = \sum_{j=g+1}^{p} \frac{P_j^o}{\mathcal{E} - E_j^o} + \sum_{i=p+1} \frac{P_i^o}{\mathcal{E} - E_i^o} \tag{4.1}$$

$$\geq \sum_{j=g+1}^{p} \frac{P_j^o}{\mathcal{E} - E_j^o} + \frac{1}{\mathcal{E} - E^o_{p+1}} \left(1 - \mathcal{O} - \sum_{j=g+1}^{p} P_j^o \right) \equiv T_o(p),$$

where it is assumed that the eigenvalues are arranged in the order $E_1^o < E_2^o < \ldots$. $T_o(p)$ is an upper bound to T_o. Hence, from (3.10) we see that

$$t_\mathcal{E}^{-1} = (V^{-1} - T_o) \leq (V^{-1} - T_o(p)) \equiv t_\mathcal{E}^{-1}(p) \tag{4.2}$$

and since it is assumed that $V > 0$,

$$t_\varepsilon^{-1}(p) \geq t_\varepsilon^{-1} > 0. \tag{4.3}$$

Since $t_\varepsilon^{-1}(p)$ and t_ε^{-1} are positive definite, the inverse operators $t_\varepsilon(p)$ and t_ε exist, are positive definite[2,9] and satisfy the inequality

$$t_\varepsilon \geq t_\varepsilon(p) > 0. \tag{4.4}$$

Better lower bounds to the reaction operator maybe gotten by introducing the idea of inner projections.[10]

Let $f = (f_1, f_2, \ldots, f_n)$ be a set of n linearly independent vectors spanning a subspace in Hilbert space having the metric $\Delta = \langle f | f \rangle$. Then the projection operator associated with this linear manifold is given by

$$Q = |f\rangle \Delta^{-1} \langle f| = \sum_{k,l} |f_k\rangle \Delta_{kl}^{-1} \langle f_l| . \tag{4.5}$$

Let $P = 1 - Q$ be the projection operator associated with the orthogonal complement to f.

The projection operator Q is positive definite since

$$\begin{aligned} \langle \Phi | Q | \Phi \rangle &= \langle \Phi | Q^2 | \Phi \rangle \\ &= \langle \Phi | Q^+ Q | \Phi \rangle = \langle Q\Phi | Q\Phi \rangle \geq 0. \end{aligned} \tag{4.6}$$

Hence, $P = 1 - Q \geq 0$ since P also is a projection operator. Therefore, Q satisfies the inequalities

$$0 \leq Q \leq 1 . \tag{4.7}$$

The reaction operator t_ε is positive definite for $\varepsilon < E^o_{g+1}$ and self-adjoint: $t_\varepsilon^+ = t_\varepsilon$. Hence, $t_\varepsilon^{\frac{1}{2}}$ exists and is positive definite.[11] The inner projection of t_ε with respect to the subspace f is given by

$$t_\varepsilon' = t_\varepsilon^{1/2} Q t_\varepsilon^{1/2} = t_\varepsilon^{1/2} |f\rangle \Delta^{-1} \langle f| t_\varepsilon^{1/2} \quad . \tag{4.8}$$

From (4.7) we find that t_ε' satisfies the inequalities

$$t_\varepsilon \geq t_\varepsilon' > 0 \quad . \tag{4.9}$$

Let us define two new manifolds g and h, where

$$g \equiv t_\varepsilon^{-1/2} f \quad , \quad h \equiv t_\varepsilon^{1/2} f \quad . \tag{4.10}$$

Substitution of these expressions into (4.8) results in the following relations:

$$t_\varepsilon' = t_\varepsilon |g\rangle \Delta^{-1} \langle g| t_\varepsilon \quad , \quad \Delta = \langle g| t_\varepsilon |g\rangle \tag{4.11}$$

and

$$t_\varepsilon' = |h\rangle \Delta^{-1} \langle h| \quad , \quad \Delta = \langle h| t_\varepsilon^{-1} |h\rangle . \tag{4.12}$$

The inner projection given by (4.11) will be called the Aronszajn projection and the space $g = (g_1, g_2, \ldots, g_n)$, the Aronszajn space. That given by (4.12) will be called the Bazley projection and the associated space $h = (h_1, h_2, \ldots, h_n)$, the Bazley space.

Löwdin[4] has shown that a lower bound to an energy level E of the Hamiltonian $\mathcal{H}$ may be obtained when there are g eigenvalues of $\mathcal{H}_o$ less than E, if the Aronszajn space g contains at least all the functions $\varphi_1^o, \varphi_2^o, \ldots, \varphi_g^o$ associated with the g unperturbed levels

and the reference function Φ is constructed by taking a linear combination of these g functions.

Replacing the reaction operator t_ε in (3.11) with the Bazley projection defined by (4.12), we have a new bracketing function

$$\mathcal{E}_1' = \langle \Phi_a^\circ | \mathcal{H}_\circ + t_\varepsilon' | \Phi_a^\circ \rangle . \tag{4.13}$$

From (4.9) we see that for $\varepsilon < E_{g+1}^\circ$,

$$\mathcal{H}_\circ + t_\varepsilon \geq \mathcal{H}_\circ + t_\varepsilon' > \mathcal{H}_\circ \tag{4.14}$$

and therefore

$$\mathcal{O}(\mathcal{H}_\circ + t_\varepsilon)\mathcal{O} \geq \mathcal{O}(\mathcal{H}_\circ + t_\varepsilon')\mathcal{O} \geq \mathcal{O}(\mathcal{H}_\circ)\mathcal{O} . \tag{4.15}$$

From this we may conclude that the eigenvalues of $\mathcal{E}_1'$ are bounded above by the eigenvalues of $\mathcal{E}_1$ and bounded below by the eigenvalues of $\mathcal{H}_\circ$ in order;

$$\mathcal{E}_{1i} \geq \mathcal{E}_{1i}' \geq E_i^\circ , \qquad (i=1,2,\ldots,g). \tag{4.16}$$

From the bracketing theorem, $\mathcal{E}_{1i}$ is a lower bound to E_i, where E_i is the i th lowest eigenvalue of $\mathcal{H}$ satisfying the criteria $E_{g+1}^\circ > \varepsilon > E_1$ and $\mathcal{O}\psi_i \neq 0$. Therefore, $\mathcal{E}_{1i}'$ is also a lower bound to the same eigenvalue. From (3.17) we observe that the eigenvalues of $\mathcal{E}_1$ are bounded above by the eigenvalues of $\mathcal{H}$ with respect to the basis Φ_a° in order. It follows at once that the latter also provide upper limits to the eigenvalues of $\mathcal{E}_1'$ in order.

More favorable upper bounds to the eigenvalues of $\mathcal{E}_1'$ may be obtained by introducing the inequality (3.16) into the expression for t_ε' which gives the result

$$t_\varepsilon' = |h\rangle\langle h|t_\varepsilon^{-1}|h\rangle^{-1}\langle h| \leq |h\rangle\langle h|V^{-1}|h\rangle^{-1}\langle h| \equiv V'$$

Hence, we have that

$$V' \geq t_\varepsilon' > 0 \ , \tag{4.17}$$

where $\lim_{\varepsilon \to \pm\infty} t_\varepsilon' = V'$ and V' is simply a Bazley projection of V onto the space spanned by the manifold h. It follows at once that

$$V \geq V' > 0 \ . \tag{4.18}$$

From (4.17) we see that

$$\mathcal{H}_0 + V' \geq \mathcal{H}_0 + t_\varepsilon' > \mathcal{H}_0 \ ;$$

hence,

$$\mathcal{O}(\mathcal{H}_0 + V')\mathcal{O} \geq \mathcal{O}(\mathcal{H}_0 + t_\varepsilon')\mathcal{O} \geq \mathcal{O}\mathcal{H}_0\mathcal{O} \ . \tag{4.19}$$

The eigenvalues of $\mathcal{E}_1'$ are bounded above by the eigenvalues of $\mathcal{H}_0 + V'$ and bounded below by the eigenvalues of $\mathcal{H}_0$:

$$h_i' \geq \mathcal{E}_{1i}' \geq E_i^0 \ , \qquad (i=1,2,\ldots,g), \tag{4.20}$$

where h_i' is the i th lowest eigenvalue of $\mathcal{H}'$ with respect to the basis $\mathcal{P}_a^0$. The inequalities given in (4.20) hold for all $\mathcal{E} < E_{g+1}^0$ and tell us at once that $\mathcal{E}_1'$ has no vertical asymptotes in this region for

any Bazley projection. The equality $\varepsilon'_{1i} = E^o_i$ occurs whenever $\mathcal{O}h = 0$: when the Bazley space is chosen orthogonal to the reference manifold $\mathcal{S}^o_a$.

The inner projected bracketing function given in (4.13) can be computed exactly in only a few cases involving particular choices of the Bazley space;[12,13,14] otherwise, T_o is truncated according to (4.1), which results in an operator $t'_\varepsilon(p)$ that, for $\varepsilon < E^o_{g+1}$, satisfies the inequalities

$$t_\varepsilon \geq t'_\varepsilon \geq t'_\varepsilon(p) > 0 \quad . \tag{4.21}$$

To remove the problem of dealing with the reduced resolvent T_o, Löwdin has suggested the substitution $h = (\varepsilon - \mathcal{H}_o)f$ be used in making the inner projection.[2] Substituting this into (4.12) we find that

$$t'_\varepsilon = (\varepsilon - \mathcal{H}_o)|f\rangle\Delta^{-1}\langle f|(\varepsilon - \mathcal{H}_o) \quad , \tag{4.22}$$

where

$$\Delta = \langle f|(\varepsilon - \mathcal{H}_o)(V^{-1} - T_o)(\varepsilon - \mathcal{H}_o)|f\rangle$$

$$= \langle f|(\varepsilon - \mathcal{H}_o)V^{-1}(\varepsilon - \mathcal{H}_o) - P(\varepsilon - \mathcal{H}_o)|f\rangle$$

since, from (2.16), $(\varepsilon - \mathcal{H}_o)T_o = (\varepsilon - \mathcal{H}_o)PT_o = P(\varepsilon - \mathcal{H}_o)T_o = P$. We shall call t'_ε defined by (4.22) the Löwdin projection and the associated space $f = (j_1, j_2, \ldots, j_n)$, the Löwdin space. This projection has the interesting property that the reduced resolvent T_o has been

eliminated from the calculation. It also leads to some very interesting behavior not observed when using the Bazley or Aronszajn projections. This behavior can be explained by the fact that the linear manifold onto which the projection of t_ε is made is itself a function of the variable ε and varies with changes in ε.

An immediate consequence of the ε dependence of the Löwdin space is that the slopes of the eigenvalue curves of $\mathcal{E}_1'$ are no longer negative definite. In fact, minima occur in these curves for values of $\varepsilon = E_i^o$, $(i=1,2,\ldots,g)$. That is, one of the eigenvalues of $\mathcal{E}_1'$ for $\varepsilon = E_k^o$, $E_k^o < E_{g+1}^o$ and $\varphi_k^o \in \varphi_a^o$, is $\mathcal{E}'_{1\ell} = E_k^o$ and E_k^o will be a minimum value of the function $\mathcal{E}'_{1\ell}$.

This is easily seen when we write down the expression for the $i\ell$ th element of $\mathcal{E}_1'$ using the Löwdin projection (4.22).

$$(\mathcal{E}_1')_{i\ell} = E_i^o \delta_{i\ell} + (\varepsilon - E_i^o)(\varepsilon - E_\ell^o)\langle \varphi_i^o | j\rangle \langle j | (\varepsilon - \mathcal{H}_o) \times V^{-1}(\varepsilon - \mathcal{H}_o) - (\varepsilon - \mathcal{H}_o)P|j\rangle^{-1}\langle j | \varphi_\ell^o\rangle \qquad (4.23)$$

$$= E_i^o \delta_{i\ell} + t'_{i\ell} .$$

The only non-vanishing term in the k th row or k th column of $\mathcal{E}_1'$ when $\varepsilon = E_k^o$ is the kk element, $(\mathcal{E}_1')_{kk} = E_k^o$. We can write the expression for (4.13) evaluated at the point $\varepsilon = E_k^o$,

$$\mathcal{E}'_1\Big|_{\mathcal{E}=E_k^o} = \begin{pmatrix} E_1^o+t'_{11} & \cdots & t'_{1k-1} & 0 & t'_{1k+1} & \cdots & t'_{1g} \\ \vdots & & \vdots & \vdots & \vdots & & \vdots \\ t'_{k-1,1} & \cdots & E_{k-1}^o+t'_{k-1,k-1} & 0 & t'_{k-1,k+1} & \cdots & t'_{k-1,g} \\ 0 & \cdots & 0 & E_k^o & 0 & \cdots & 0 \\ t'_{k+1,1} & \cdots & t'_{k+1,k-1} & 0 & E_{k+1}^o+t'_{k+1,k+1} & \cdots & t'_{k+1,g} \\ \vdots & & \vdots & \vdots & \vdots & & \vdots \\ t'_{g,1} & \cdots & t'_{g,k-1} & 0 & t'_{g,k+1} & \cdots & E_g^o+t'_{gg} \end{pmatrix} . \tag{4.24}$$

Obviously, E_k^o is an eigenvalue of $\mathcal{E}'_1$ for $\mathcal{E} = E_k^o$. That this is also a minimum in some eigenvalue curve, e.g., $\mathcal{E}'_{1\ell}$, of $\mathcal{E}'_1$ is seen by looking at the first and second derivatives of $\mathcal{E}'_1$ with respect to $\mathcal{E}$ evaluated at $\mathcal{E} = E_k^o$. If $\mathcal{E}'_{1\ell} = E_k^o = \mathcal{E}$, then

$$\left.\frac{d\mathcal{E}'_{1\ell}}{d\mathcal{E}}\right|_{\mathcal{E}=E_k^o} = 0 \quad , \quad \left.\frac{d^2\mathcal{E}'_{1\ell}}{d\mathcal{E}^2}\right|_{\mathcal{E}=E_k^o} > 0$$

are sufficient criteria for the point $\mathcal{E} = E_k^o$ to be a minimum in the $\mathcal{E}'_{1\ell}$ curve. From (3.21) we know that

$$\frac{d\mathcal{E}'_{1\ell}}{d\mathcal{E}} = \mathbb{C}_\ell^+ \left.\frac{d\mathcal{E}'_1}{d\mathcal{E}}\right|_{\mathcal{E}=E_k^o} \mathbb{C}_\ell \quad , \tag{4.25}$$

where $\mathcal{C}_\ell$ is the normalized eigenvector of $\mathcal{E}_1'$ associated with the eigenvalue E_k°. Since

$$\mathcal{C}_\ell = \begin{pmatrix} 0 \\ \vdots \\ 0 \\ 1_k \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$

is the eigenvector for $\mathcal{E}_{1\ell}' = E_k^\circ = \mathcal{E}$, it follows from (4.25) that

$$\left.\frac{d\mathcal{E}_{1\ell}'}{d\mathcal{E}}\right|_{\mathcal{E}=E_k^\circ} = (0 \ldots 01_k 0 \ldots 0) \left.\begin{pmatrix} \frac{d\mathcal{E}_1'}{d\mathcal{E}} \end{pmatrix}\right|_{\mathcal{E}=E_k^\circ} \begin{pmatrix} 0 \\ \vdots \\ 0 \\ 1_k \\ 0 \\ \vdots \\ 0 \end{pmatrix}$$

$$= \left.\left|\frac{d\mathcal{E}_1'}{d\mathcal{E}}\right|_{kk}\right|_{\mathcal{E}=E_k^\circ} \tag{4.26}$$

From (4.23) and the identity $\frac{d\Delta^{-1}}{d\eta} = -\Delta^{-1}\frac{d\Delta}{d\eta}\Delta^{-1}$, we obtain the expression

$$\left|\frac{d\mathcal{E}_1'}{d\mathcal{E}}\right| = \Big[2(\mathcal{E}-E_k^\circ)\langle\varphi_k^\circ|j\rangle\Delta^{-1}\langle j|\varphi_k^\circ\rangle - \tag{4.27}$$

$$(\mathcal{E}-E_k^\circ)^2\langle\varphi_k^\circ|j\rangle\Delta^{-1}\frac{d\Delta}{d\mathcal{E}}\Delta^{-1}\langle j|\varphi_k^\circ\rangle\Big],$$

from which it follows that

$$\left.\frac{d\mathcal{E}_{1\ell}'}{d\mathcal{E}}\right|_{\mathcal{E}=E_k^\circ} = \left.\left|\frac{d\mathcal{E}_1'}{d\mathcal{E}}\right|_{kk}\right|_{\mathcal{E}=E_k^\circ} = 0. \tag{4.28}$$

The expression for the second derivative is given by

$$\left.\frac{d^2\mathcal{E}'_{12}}{d\varepsilon^2}\right|_{\varepsilon=E_k^\circ} = C_l^\dagger \left.\frac{d^2\mathcal{E}'_1}{d\varepsilon^2}\right|_{\varepsilon=E_k^\circ} C_l = \left.\left(\frac{d^2\mathcal{E}'_1}{d\varepsilon^2}\right)_{kk}\right|_{\varepsilon=E_k^\circ}$$

$$= \Big[2\langle\varphi_k^\circ|f\rangle \Delta^{-1}\langle f|\varphi_k^\circ\rangle - 4(\varepsilon-E_k^\circ)\langle\varphi_k^\circ|f\rangle$$

$$\times \Delta^{-1}\frac{d\Delta}{d\varepsilon}\langle f|\varphi_k^\circ\rangle - (\varepsilon-E_k^\circ)^2\langle\varphi_k^\circ|f\rangle$$

$$\times \frac{d}{d\varepsilon}\left\{\Delta^{-1}\frac{d\Delta}{d\varepsilon}\Delta^{-1}\right\}\langle f|\varphi_k^\circ\rangle\Big]\Big|_{\varepsilon=E_k^\circ}$$

$$= 2\langle\varphi_k^\circ|f\rangle\Delta^{-1}\langle f|\varphi_k^\circ\rangle \quad > 0. \qquad (4.29)$$

Hence, from (4.28) and (4.29) it is obvious that the g curves of $\mathcal{E}'_1$ using the Löwdin projection are no longer monotonically descending.

In general, the curve $\mathcal{E}'_{1\ell}$ can have minima and cross the $\mathcal{E}'_1 = \varepsilon$ line at several of the points $\varepsilon = E_i^\circ$. It may also cross the $\mathcal{E}'_1 = \varepsilon$ line at values of ε not eigenvalues of $\mathcal{H}_o$. From (4.20) we have the relation $h'_\ell \geq \mathcal{E}'_{1\ell} \geq E_\ell^\circ$ for any $\varepsilon < E_{g+1}^\circ$. It follows that $\mathcal{E}'_{1\ell}$ can have minima at any or all the points $\varepsilon = E_i^\circ$, where $i \geq \ell$ and $E_i^\circ \leq h'_\ell$. These features of the Löwdin projection are developed further in the application of this theory to He and Li^+.

In this section, we have developed a procedure for calculating lower bounds to the eigenvalues of a Hamiltonian $\mathcal{H} = \mathcal{H}_o + V$, where

$V > 0$, and $\mathcal{H}_o$ has a set of known eigenfunctions. The subspace $\mathcal{P}_a^o$ is chosen such that $\mathcal{O}\,\psi_i \neq 0$, where ψ_i is the eigenfunction of $\mathcal{H}$ associated with the i th lowest eigenvalue E_i having a particular symmetry and such that it contains all the eigenfunctions associated with eigenvalues of $\mathcal{H}_o$ less than E_i having the same symmetry as ψ_i. The Löwdin space $\mathcal{J}$ must be chosen such that the overlap integrals $\langle \varphi_i^o | j_k \rangle$ with the functions of the reference manifold $\mathcal{P}_a^o$ are non-zero. It is then a rather straightforward matter to calculate the matrix elements given in (4.23). If $\mathrm{Tr}(\mathcal{O}) = g$, then by choosing the parameter $\mathcal{E} > E_i$ and $< E_{g+1}^o$, the i th lowest solution of the secular equation

$$\left| \mathcal{E}' - \mathcal{E}' \mathbb{1} \right| = 0 \tag{4.30}$$

provides a lower bound to E_i.

CHAPTER V

LOWER BOUNDS TO THE ^3S STATES OF He AND Li^+

The procedure discussed in Chapter IV is used to calculate lower bounds to some of the low-lying ^3S states of He and Li^+. For the two-electron series, the nonrelativistic Hamiltonian in atomic units is given by

$$\mathcal{H} = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \frac{z}{r_1} - \frac{z}{r_2} + \frac{1}{r_{12}} \quad , \tag{5.1}$$

where z is the nuclear charge, $\vec{r}_1$ and $\vec{r}_2$ are the position vectors of the electrons, $r_i = |\vec{r}_i|$, i = 1, 2 and $r_{12} = |\vec{r}_1 - \vec{r}_2|$.

We will take advantage of the symmetry properties of the Hamiltonian (5.1) and restrict ourselves to states having ^3S symmetry. For these states, the eigenfunctions of (5.1) depend only on r_1, r_2 and r_{12} and are antisymmetric in the spatial coordinates of the two electrons, that is

$$P_{12}\,\psi(\vec{r}_1, \vec{r}_2) = -\psi(\vec{r}_1, \vec{r}_2) \quad , \tag{5.2}$$

where P_{12} is the permutation operator acting on the coordinates $\vec{r}_1$ and $\vec{r}_2$.

The Hamiltonian (5.1) may be separated into an unperturbed part $\mathcal{H}_0$ and a positive definite perturbation V, where

$$\mathcal{H}_0 = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \frac{z}{r_1} - \frac{z}{r_2} \quad , \tag{5.3}$$

$$V = \frac{1}{r_{12}} > 0 \quad .$$

The eigenfunctions of $\mathcal{H}_o$ are well known and for the ^3S symmetry are given by

$$\varphi^o_{m_1 m_2 \ell} = C_{m_1 m_2 \ell}\left[R_{m_1\ell}(r_1)\,R_{m_2\ell}(r_2) - R_{m_1\ell}(r_2)\,R_{m_2\ell}(r_1)\right] P_\ell(\cos\theta_{12}), \tag{5.4}$$

where the $R_{n_i\ell}$ are normalized hydrogen radial wave functions, P_ℓ is the ℓ th normalized Lengendre polynomial and θ_{12} is the angle between the radial vectors r_1 and r_2. The $C_{n_1 n_2 \ell}$ are chosen in such a way that the $\varphi^o_{n_1 n_2 \ell}$ are normalized to π^2,

$$\langle \varphi^o_{m_1 m_2 \ell} \mid \varphi^o_{m_1 m_2 \ell} \rangle = \pi^2 . \tag{5.5}$$

The eigenvalue spectrum for the ^3S levels of $\mathcal{H}_o$ is given by

$$E^o_{m_1 m_2} = -\frac{Z^2}{2}\left[\frac{1}{m_1^2} + \frac{1}{m_2^2}\right] . \tag{5.6}$$

For the lowest ordered ^3S states of $\mathcal{H}_o$, one electron is in the n = 1 level and the angular momentum L^2 has the eigenvalue zero, $\ell = 0$. The eigenfunctions and eigenvalues of $\mathcal{H}_o$ are then given by

$$\varphi^o_i = \frac{1}{4\sqrt{2}}\left[R_{10}(r_1)\,R_{i+1,0}(r_2) - R_{10}(r_2)\,R_{i+1,0}(r_1)\right] , \tag{5.7}$$

$$E^o_i = -\frac{Z^2}{2}\left[1 + \frac{1}{(i+1)^2}\right] , \quad (i=1,2,\ldots) .$$

By including in the reference manifold $\mathcal{P}^o_a$ only those functions φ^o_i having ^3S symmetry, we obtain from (4.30) lower bounds only to those states of $\mathcal{H}$ having this same symmetry since $\mathcal{O}\psi = 0$ for any state ψ of $\mathcal{P}$ not having ^3S symmetry. Hence, the solutions of (4.30) will be in order lower bounds to the 2^3S, 3^3S, 4^3S, ..., j^3S states of $\mathcal{H}$, i.e.,

for $\mathcal{E} < E^{o}_{g+1}$ and $\mathcal{E} > E_{j^3S}$,

$$\mathcal{E}'_{11} < E_{2^3S} \;,\quad \mathcal{E}'_{12} < E_{3^3S} \;,\quad \cdots \;,\quad \mathcal{E}'_{1j+1} < E_{j^3S} \;.$$

With the solutions of $\mathcal{H}_o$ available for the construction of the reference manifold φ^{o}_{a}, we must next select the functions for the Löwdin space $\mathcal{J}$. It has already been pointed out in Chapter IV that the choice of functions for the $\mathcal{J}$ manifold should be made subject to the condition that the overlap integrals $\langle \varphi^{o}_{i} | j_k \rangle$ be non-zero. Functions satisfying the criteria that

$$\begin{aligned} P_{12}\, j_k &= -j_k \;, \\ L^2\, j_k &= 0 \;, \end{aligned} \tag{5.8}$$

where L^2 is the angular momentum operator, can satisfy these conditions.

The functions were selected on the basis of those introduced by Hylleraas[15] and are given by

$$j_i = C_{k_i l_i m_i}\, e^{-\eta s}\, s^{k_i}\, t^{2l_i+1}\, u^{m_i} \;, \tag{5.9}$$

where η is an arbitrary scaling parameter and

$$s = r_1 + r_2 \;,\quad t = r_1 - r_2 \;,\quad u = r_{12} \;. \tag{5.10}$$

The $C_{k_i l_i m_i}$ are normalization constants selected in such a way that the functions given by (5.9) are normalized to $16\pi^2$. This choice of normalization proves to be convenient in the calculation. It is easily seen that the functions given by (5.9) satisfy the criteria (5.8).

The minimum size of the reference manifold is determined by the number of states of $\mathcal{H}_0$ having the same symmetry as and eigenvalues less than those of the state of $\mathcal{H}$ to which a lower bound is sought.

For the ^3S states of He the ordering in atomic units (a.u.) is given by

$$E_1^o = -2.500 \ldots < E_2^o = -2.22 \ldots < E_{2^3S} = -2.175229 \ldots \text{[16,17]} <$$
$$E_3^o = -2.1250 \ldots < E_4^o = -2.080 \ldots < E_{3^3S} = -2.0687 \ldots \text{[18]} <$$
$$E_5^o = -2.05050 \ldots \qquad (5.11)$$

and for Li^+,

$$E_1^o = -5.6250 \ldots < E_{2^3S} = -5.110727 \ldots \text{[19]} < E_2^o = -5.00 \ldots <$$
$$E_3^o = -4.781250 \ldots < E_{3^3S} = -4.752 \ldots \text{[18]} < E_4^o = -4.68 \ldots <$$
$$E_{4^3S} = -4.637 \ldots \text{[18]} < E_5^o = -4.6250 \ldots \quad . \qquad (5.12)$$

From (5.11) it follows that, to calculate a lower bound using (4.30) to the 2^3S state of He, we must at least include φ_1^o and φ_2^o in the reference manifold $\mathcal{P}_a^o$, i.e., g = 2 and for a lower bound to the 3^3S state we must choose g = 4, i.e., $\mathcal{P}_a^o = \varphi_1^o, \varphi_2^o, \varphi_3^o, \varphi_4^o$. From (5.12) we see that, to obtain lower bounds to the 2^3S, 3^3S and 4^3S levels of Li^+, it is necessary to have g = 1, 3 and 4 respectively. Of course, as many additional functions as desired may be included but these values of g give the minimum sizes of the reference manifolds necessary in order to calculate lower bounds by this procedure to the levels indicated.

The size of the Löwdin space, which shall be denoted by NINT, can vary from one to all the functions of a complete set. If the set is complete, then the exact eigenvalues of $\mathcal{H}$ are found to be those

values of $\mathcal{E}$ at which the curves $\mathcal{E}'_{1i}$ cross the $\mathcal{E}'_1 = \mathcal{E}$ line. In general, however, this set is finite and the curves cross the $\mathcal{E}'_1 = \mathcal{E}$ line at the eigenvalues of $\mathcal{H}_o$ associated with functions in the reference manifold. Crossing may also occur for values of $\mathcal{E} \neq E^o_i$, $i < g + 1$.

Once the reference and internal projection manifolds are chosen, the matrix elements of $\mathcal{E}'_1$, given by (4.23), may be found and the secular equation (4.30) solved. Both of the parameters η and $\mathcal{E}$ are varied to give a maximum in each of the g lower bound curves, where the variation of $\mathcal{E}'_1$ with respect to $\mathcal{E}$ is subject to the condition that $\mathcal{E}$ be greater than the energy of the state to which a lower bound is desired and less than E^o_{g+1}. The computation procedures involved will be discussed in the Appendix.

We see in Table 1 the lower bounds obtained by this procedure using 40 functions of the type given in (5.8) to construct the Löwdin projection, where the restrictions $k_i = 0, 1, 2$, $\ell_i = 0, 1, 2, 3, 4$, $m_i = 0, 1, 2$ and $k_i + m_i \leq 3$ were imposed on the powers of the variables s, t and u respectively.

Lower bounds were calculated for the 2^3S level of He by taking the size of the reference manifold to be g = 2 and g = 4, and for the 2^3S level of Li^+ by taking g = 1 and g = 4. Since the size of the reference manifold determines the size of the secular equation, a fourth order equation is the largest to be solved. From the results in Table 1 we observe that, so long as all the eigenfunctions of $\mathcal{H}_o$ associated with eigenvalues less than the 2^3S level of $\mathcal{H}$ are included

TABLE 1

OPTIMUM LOWER BOUNDS TO SOME OF THE ^3S STATES OF He AND Li^+ FOR NINT = 40

State Symbol	g	Z	Upper bound (a.u.)	ε (a.u.)	η	Lower bound (a.u.)	Separation between upper and lower bound
2^3S	4	2	-2.175229[a]	-2.1752	1.35	-2.17527[b]	.00004
2^3S	2	2	-2.175229[a]	-2.1752	1.40	-2.17529[b]	.00006
3^3S	4	2	-2.0687[c]	-2.056	1.15	-2.0867	.018
2^3S	4	3	-5.110727[d]	-5.1107	2.12	-5.11076[b]	.00003
2^3S	1	3	-5.110727[d]	-5.1107	2.14	-5.11076[b]	.00003
3^3S	4	3	-4.752[c]	-4.660	2.00	-4.757	.005
4^3S	4	3	-4.637[c]	-4.626	1.90	-4.691	.054

[a] See reference 16 and 17

[b] Due to roundoff, the 5 th place after the decimal is uncertain by ± 1.

[c] See reference 18.

[d] See reference 19.

in $\mathcal{G}_a^o$, little improvement is found when more reference functions are added. The magnitudes of the errors in the bounds to the higher states are seen to be much greater than that of the 2^3S state in both the He and Li^+ calculations. This is, however, not an unexpected result. It has been pointed out by Löwdin[7] that a truncated set which works well enough for the ground state may give a surprisingly poor result for even the first excited state of the same symmetry.

Quite good lower bounds have been calculated by Pekeris[17] to the 2^3S state of He using Temple's method.[20] By solving a determinant of order 252, he obtained a lower bound of -2.175239 a.u. The lower bound to this state, for g = 4, which is given in Table 1, is very close to this value. In order to obtain a lower bound to an energy level of H using Temple's formula, it is necessary to calculate matrix elements of H^2 and to have a knowledge of the next higher level of the system. It is apparent from the work of Pekeris that in order to obtain a good lower bound using Temple's formula, the size of the secular equation must be very large.

Goscinski[21] has shown in his dissertation that Temple's formula can be derived from (2.19) for g = 1.

Miller[22] has obtained lower bounds to the low-lying ^3S states of He using the method of intermediate Hamiltonians.[23] Solving a secular equation of order 9, he calculated lower bounds to the 2^3S and 3^3S levels of -2.1802 a.u. and -2.0704 a.u. respectively. His result for the 3^3S state is somewhat better than that given in Table 1. Goscinski[21] has shown that Miller's equation can be derived from an

expression for the bracketing function $\mathcal{E}'_1$ using a truncated resolvent $T_o(p)$ as is given in (4.1) and that the points $\mathcal{E} = \mathcal{E}_{1k}$ correspond to its solutions. By making this truncation, however, one reduces the contribution from the continuum, a problem that is eliminated in using the Löwdin projection.

A study was made to determine the behavior of the lower bound curves when the scaling parameter η is fixed and $\mathcal{E}$ is permitted to vary over a wide range of values. For both He and Li^+, g was taken to be 4 and NINT to be 40. In Chapter IV we observed that the Löwdin projection greatly changes the character of the lower bound curves from that shown in Fig. 2 for example. We found that, using this projection, a minimum appears in one of the lower bound curves at each of the points where $\mathcal{E}$ equals an eigenvalue of $\mathcal{H}_o$ associated with an eigenfunction in the reference manifold. This behavior is shown in Figs. 3 and 4. These figures demonstrate the effect the Löwdin projection has on the eigenvalue curves of $\mathcal{E}'_1$.

It is interesting to examine the effect that changing the number of internal projection functions in the Löwdin space has on these curves. Of course, using fewer functions in constructing the projection t'_ε will result in a poorer approximation to the reaction matrix t_ε. Keeping $\eta = 1.2$, the results of using NINT = 20 and NINT = 10 are shown in Figs. 5 and 6 respectively.

We observe in Fig. 5 that the lowest bracketing curve $\mathcal{E}'_{11}$ does not recross the $\mathcal{E}'_1 = \mathcal{E}$ line after the minimum at $\mathcal{E} = E^o_2$, as it does in Fig. 3 and the minimum at $\mathcal{E} = E^o_3$ occurs in the $\mathcal{E}'_{13}$ curve and not

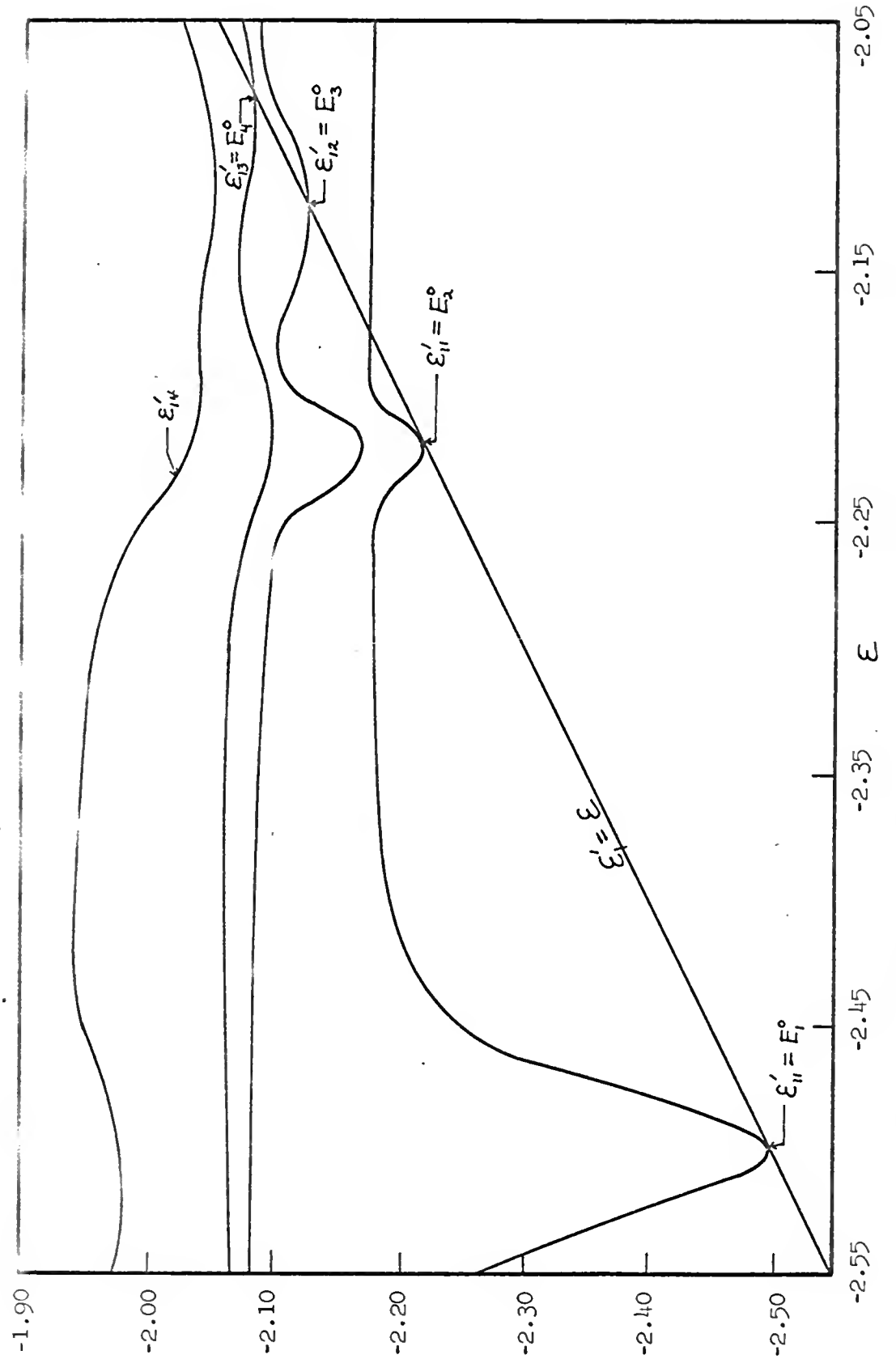

Fig. 3. Lower bound curves of He for g = 4, NINT = 40 and η = 1.2.

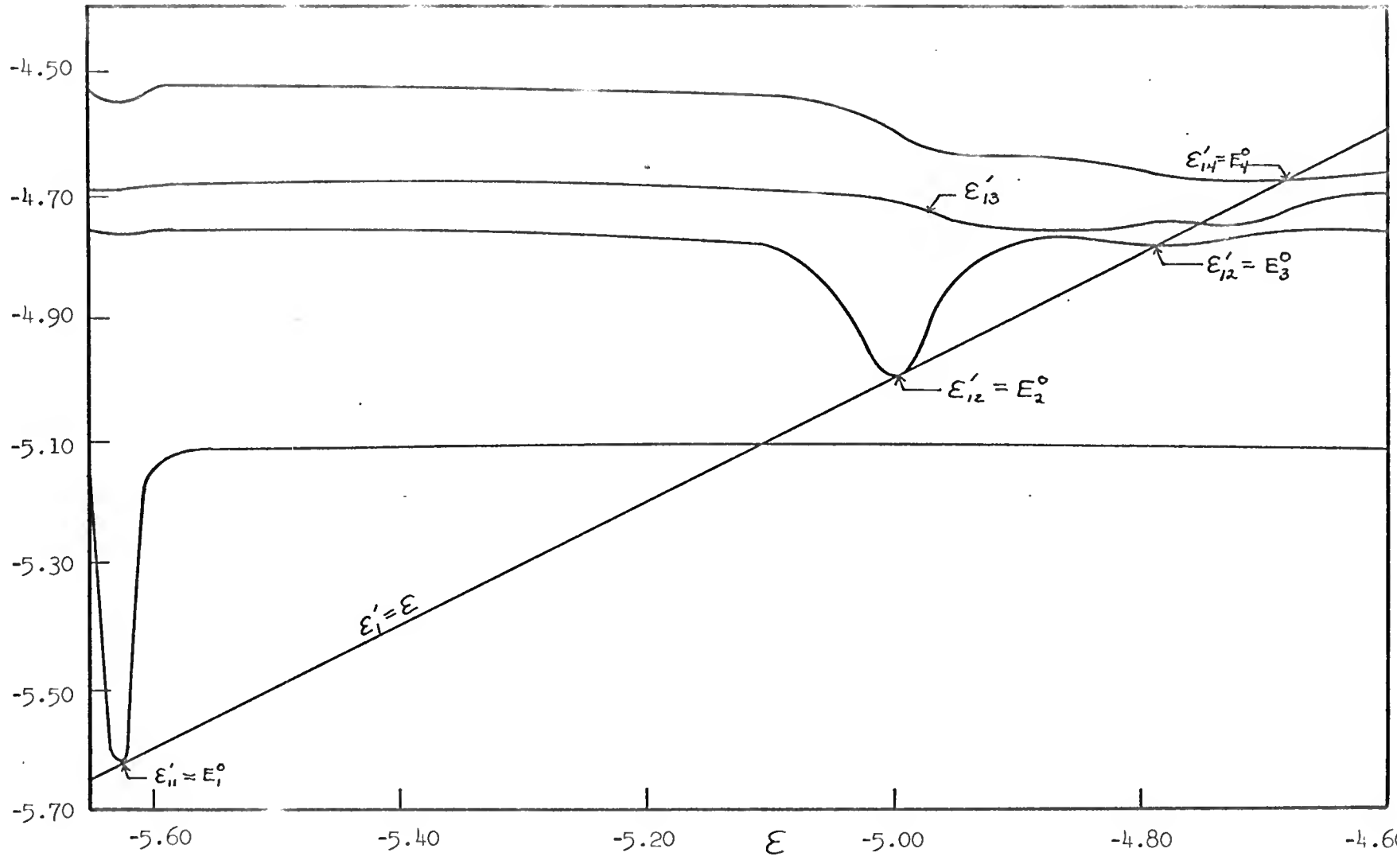

Fig. 4. Lower bound curves of Li^+ for g = 4, NINT = 40 and η = 2.1.

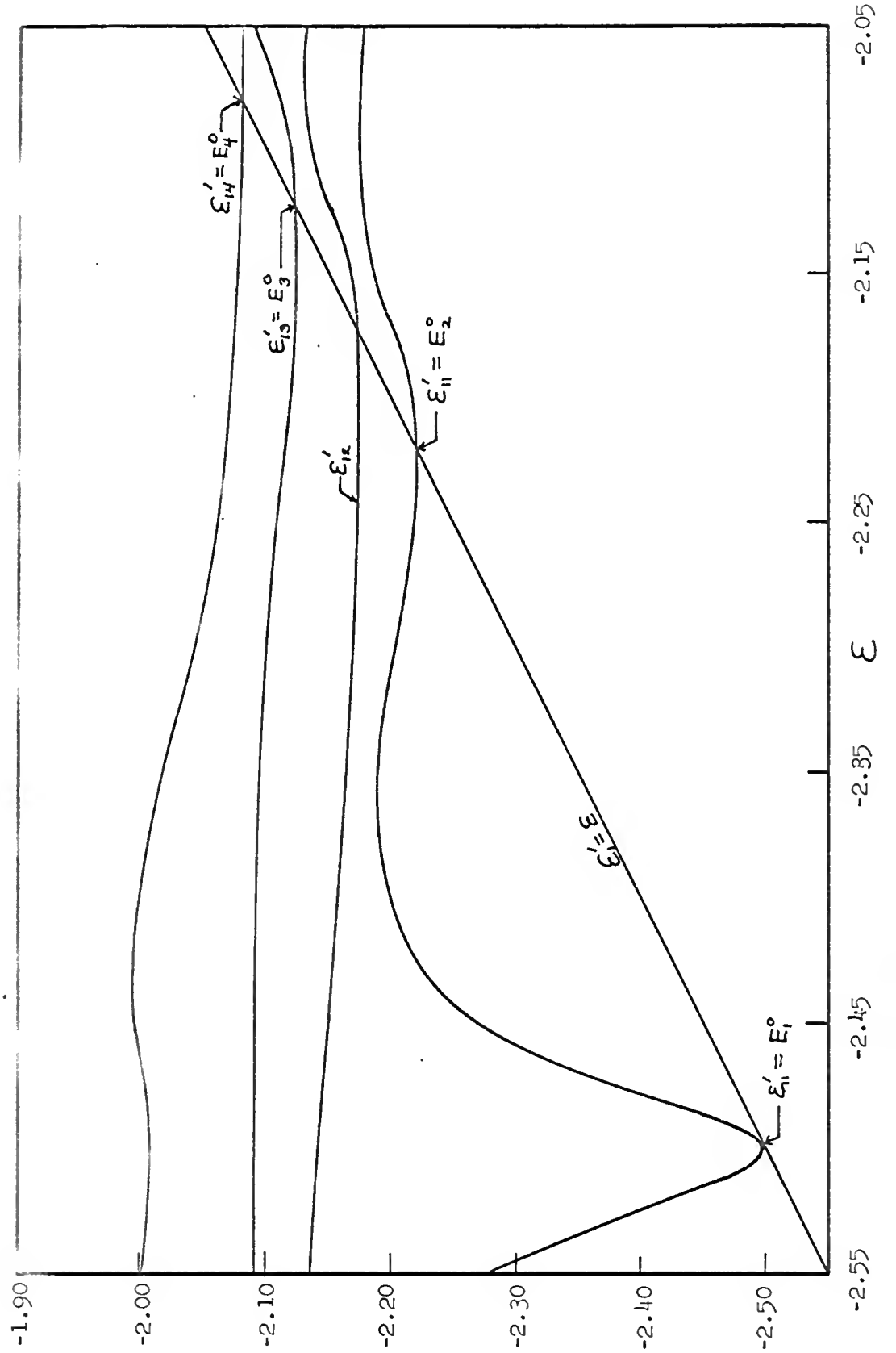

Fig. 5. Lower bound curves of He for g = 4, NINT = 20 and η = 1.2.

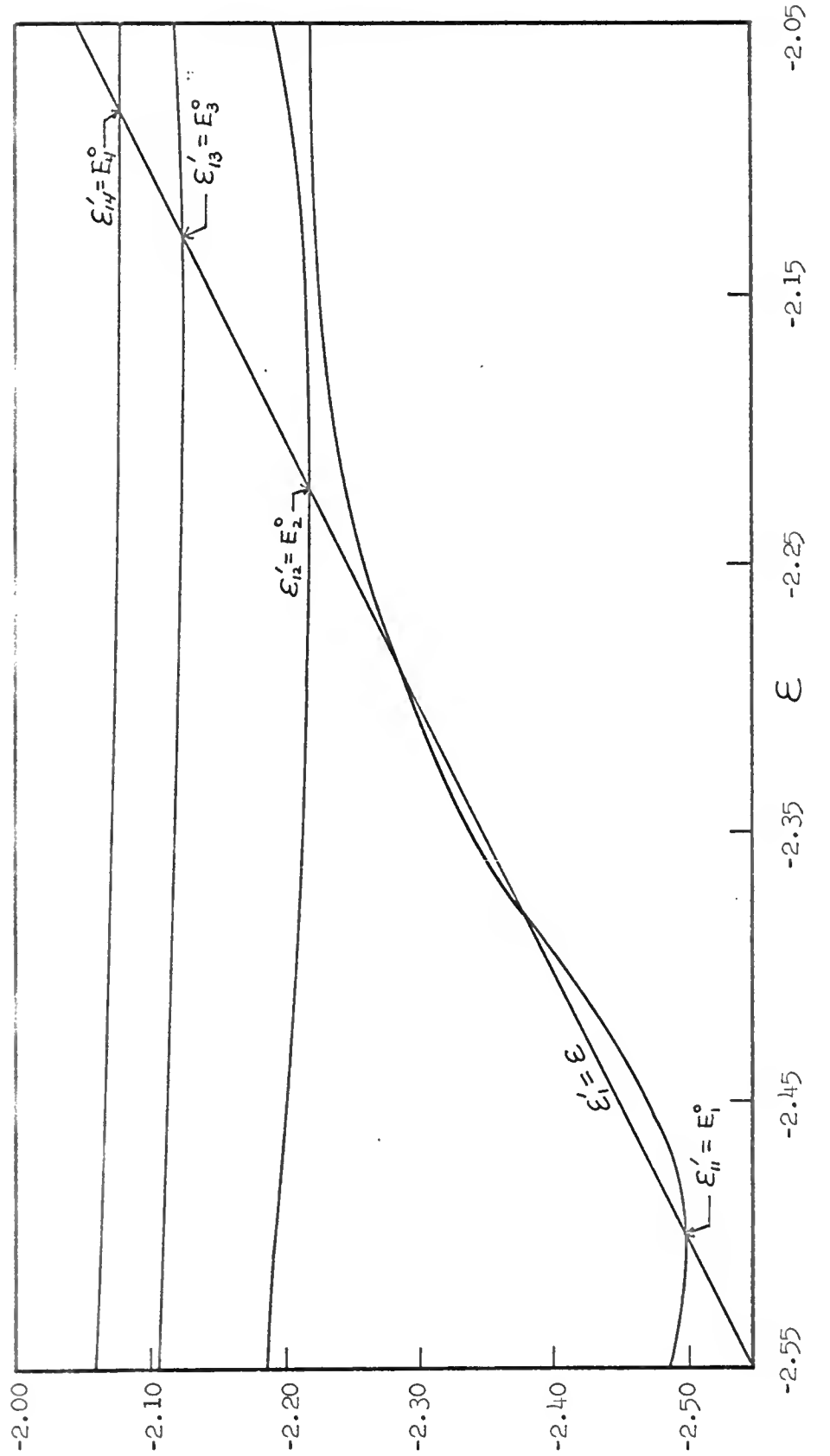

Fig. 6. Lower bound curves of He for g = 4, NINT = 10 and η = 1.2.

in the $\mathcal{E}'_{12}$ curve as it does in Fig. 3. In Fig. 6, we find that using only 10 functions to construct the Löwdin projection results in the minimum at $\mathcal{E} = E_2^{\sim}$ being shifted from the $\mathcal{E}'_{11}$ to the $\mathcal{E}'_{12}$ curve. It is also apparent that the $\mathcal{E}'_{12}$, $\mathcal{E}'_{13}$ and $\mathcal{E}'_{14}$ curves vary only slightly from the unperturbed eigenvalues E_2^o, E_3^o and E_4^o respectively, over the region under consideration. Only the $\mathcal{E}'_{11}$ curve is appreciably affected by t'_ε .

For NINT = 10, we find, by permitting η to vary, that the minimum for $\mathcal{E} = E_2^o$ is shifted back to the $\mathcal{E}'_{11}$ curve for $\eta = 1.35$. For $\eta = 1.35$ and $\mathcal{E} = -2.06$, the lower bound to the 2^3S state of He is -2.216 a.u. These results are shown in Fig. 7.

We conclude this study of the lower bound curves by noting that, if the Löwdin projection provides an adequate approximation to the reaction operator t_ε , the i th lower bound curve will have minimums at each point $\mathcal{E} = E_j^o$, where $E_{i-1} < E_j^o < E_i$ and will cross the $\mathcal{E}'_1 = \mathcal{E}$ line for the last time for some value of $\mathcal{E}$ not an eigenvalue of $\mathcal{H}_o$. If the set onto which the projection is being made is complete, this latter crossing will occur at the eigenvalue E_i of $\mathcal{H}$.

This behavior is observed in Fig. 3 where the $\mathcal{E}'_{11}$ curve has minima for $\mathcal{E} = E_1^o$ and $\mathcal{E} = E_2^o$ and crosses the $\mathcal{E}'_1 = \mathcal{E}$ line finally for $\mathcal{E} = -2.1753$. From (5.11) $E_{2^3S} < E_3^o < E_4^o < E_{3^3S}$; hence, the $\mathcal{E}'_{12}$ curve should have minima for $\mathcal{E} = E_3^o$, E_4^o if this projection adequately represents the reaction operator. We see in Fig. 3 that the $\mathcal{E}'_{12}$ curve crosses the $\mathcal{E}'_1 = \mathcal{E}$ line only once, at the minimum $\mathcal{E}'_{12} = \mathcal{E} = E_3^o$. The minimum for $\mathcal{E} = E_4^o$ appears instead in the $\mathcal{E}'_{13}$ curve. From the results in Table 1, we see that $\mathcal{E}'_{12}$ provides a much poorer lower bound to the 3^3S state than $\mathcal{E}'_{11}$ does to the 2^3S state of He.

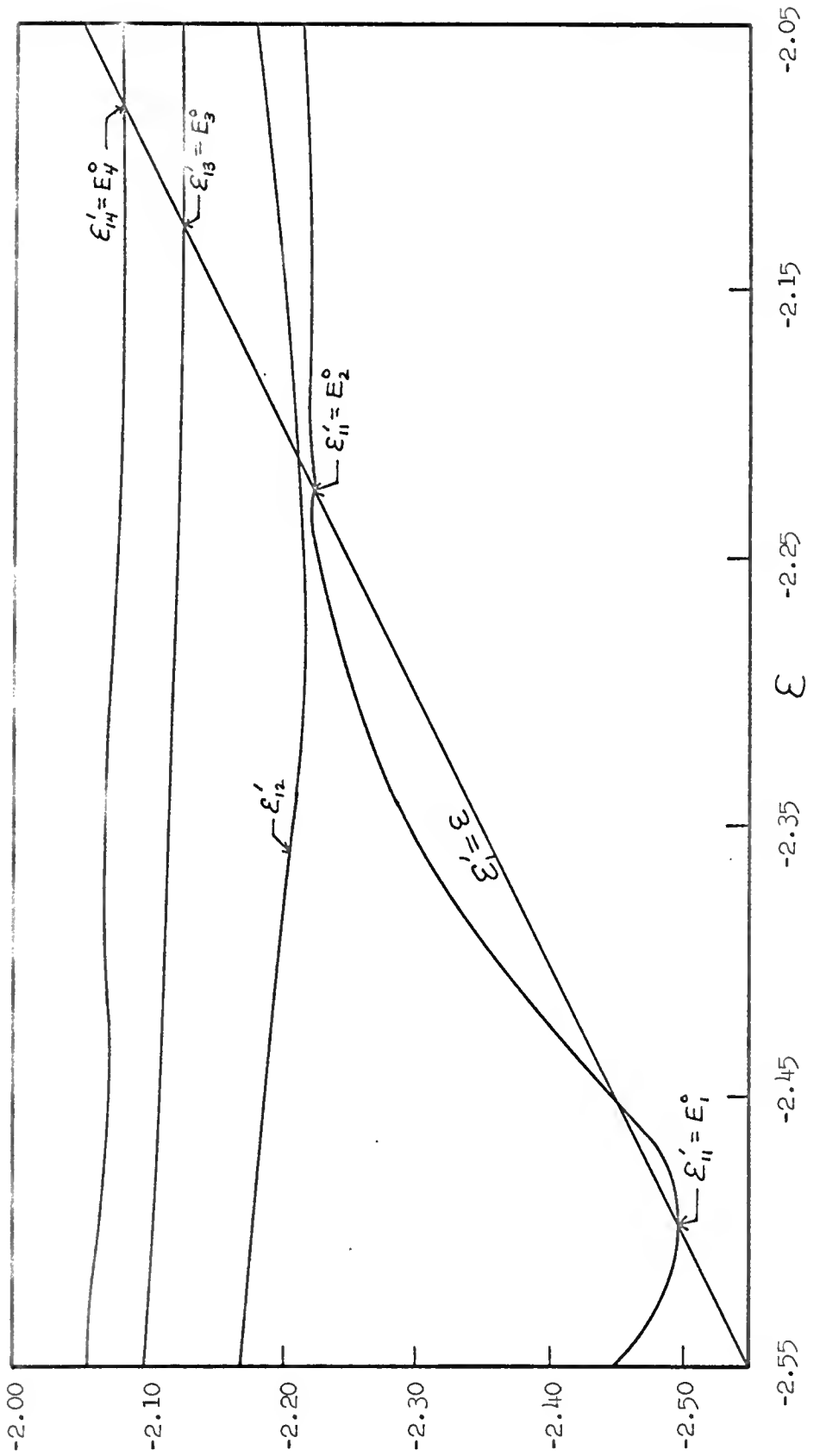

Fig. 7. Lower bound curves of He for g = 4, NINT = 10 and η = 1.35.

A similar analysis can be made of the Li^+ curves shown in Fig. 4 and the He curves shown in Figs. 5, 6, and 7.

Although the choice of functions of the type (5.9) used to construct the Löwdin projection is perhaps not the best possible selection, the bracketing curves obtained using this choice illustrate the general behavior we may expect when using this projection and the material discussed in Chapter IV.

APPENDIX

This is an outline of the procedures used in the calculations of Chapter V.

The calculation of the Löwdin projection (4.22) and the matrix $\mathcal{E}_1'$ (4.13) require the evaluation of the quantities $\mathcal{H}_o j_i$, i=1,2,..., 40, and the Δ matrix whose matrix elements are given by

$$\Delta_{kl} = \varepsilon^2 \langle j_k | V^{-1} | j_l \rangle - \varepsilon \{ \langle j_k | j_l \rangle + \langle V^{-1} j_k | \times \mathcal{H}_o j_l \rangle + \langle \mathcal{H}_o j_k | V^{-1} j_l \rangle \} + \langle j_k | \mathcal{H}_o | j_l \rangle + \langle \mathcal{H}_o j_k | V^{-1} | \mathcal{H}_o j_l \rangle + \sum_{i=1}^{g} (\varepsilon - E_i^o) \langle j_k | \varphi_i^o \rangle \langle \varphi_i^o | j_l \rangle , \tag{A.1}$$

where g = 4.

The Hamiltonian $\mathcal{H}_o$ and the inverse of the perturbation V^{-1}, defined by (5.3), may be expressed in terms of the corrdinates S, t and u:[24]

$$V^{-1} = u , \tag{A.2}$$

$$\mathcal{H} = -\left[\frac{\partial^2}{\partial s^2} + \frac{\partial^2}{\partial t^2} + \frac{4s}{s^2-t^2} \frac{\partial}{\partial s} - \frac{4t}{s^2-t^2} \frac{\partial}{\partial t} - \frac{2st^2}{u(s^2-t^2)} \times \frac{\partial^2}{\partial u \partial s} + \frac{2su}{s^2-t^2} \frac{\partial^2}{\partial u \partial s} + \frac{2s^2 t}{u(s^2-t^2)} \frac{\partial^2}{\partial u \partial t} - \frac{2tu}{s^2-t^2} \times \frac{\partial^2}{\partial u \partial t} + \frac{\partial^2}{\partial u^2} + \frac{2}{u} \frac{\partial}{\partial u} + \frac{4zs}{s^2-t^2} \right] . \tag{A.3}$$

From (A.3) and (5.9) we see that $\mathcal{H}_0$ operating on the functions j_i gives a linear combination of terms having the form

$$(s^2-t^2)^n s^k t^{2l+1} u^m e^{-\eta s} \quad , \tag{A.4}$$

where n = -1, 0, $k \geq 0$, $l \geq 0$ and $m \geq -1$.

From this we can see that the matrix elements of (A.1) involving only functions of the Löwdin space are simply linear combinations of integrals of the type

$$(n,k,l,m) = 2\pi^2 \int_0^\infty e^{-2\eta s} s^k ds \int_0^s u^m du \int_0^u (s^2-t^2)^n t^{2l} dt \, , \tag{A.5}$$

where n = -1, 0, 1, $k \geq 0$, $l \geq 0$ and $m \geq 0$. These integrals may all be evaluated in closed form:[25]

$$(0,k,l,m) = 2\pi^2 \frac{(k+2l+m+2)!}{(2l+1)(2l+m+2)} \cdot \frac{1}{(2\eta)^{k+2l+m+3}} \, , \tag{A.6}$$

$$(1,k,l,m) = 2\pi^2 \frac{(k+2l+m+4)!}{(2\eta)^{k+2l+m+5}} \left\{ \frac{1}{(2l+1)(2l+m+2)} - \frac{1}{(2l+3)(2l+m+4)} \right\} , \tag{A.7}$$

$$(-1,k,l,m) = 2\pi^2 \frac{(k+2l+m)!}{(2\eta)^{k+2l+m+1}} \left\{ (2m+2)^{-1} \sum_{\nu=1}^{m} \left[\frac{1+(-1)^{m-\nu}}{\nu} + (1+(-1)^m) \ln 2 \right] - \sum_{\mu=0}^{l-1} \left\{ (2l+m-2\mu)(2l-2\mu-1) \right\}^{-1} \right\} . \tag{A.8}$$

The integrals involving functions of the reference manifold and the Löwdin space $\langle \varphi_j^o | j_k \rangle$ can be expressed as a linear combination of integrals of the type

$$(a,b,k,l,m) = \pi^2 \int_0^\infty e^{-as} s^k ds \int_0^s u^m du \int_{-u}^{u} (s^2-t^2) t^l e^{-bt} dt, \tag{A.9}$$

where $l \geq 0$, $k \geq 0$ and $m \geq 0$. The solution to this type of integral is also known in closed form[5] and is given by

$$(a,b,k,l,m) = \pi^2 \frac{l!}{b^{l+m+2}} \sum_{p=0}^{l} \frac{(p+m)!}{p!} \sum_{q=0}^{p+m} \frac{(q+k)!}{q!} b^q \left\{ \right.$$

$$\frac{1}{(a+b)^{q+k+1}} \left[\frac{(q+k+2)(q+k+1)}{(a+b)^2} - \frac{(l+2)(l+1)}{b^2} \right] +$$

$$\left. \frac{(-1)^{m+q}}{(a-b)^{q+k+1}} \left[\frac{(q+k+2)(q+k+1)}{(a-b)^2} - \frac{(l+2)(l+1)}{b^2} \right] \right\} -$$

$$\frac{(l+2)!}{b^{l+m+4}} \sum_{q=0}^{p+m} \frac{(q+k)!}{q!} b^q \left\{ \frac{1}{(a+b)^{q+k+1}} + \right.$$

$$\left. \frac{(-1)^{m+q}}{(a-b)^{q+k+1}} \right\} + \left\{ 1 + (-1)^m \right\} \frac{l!\,k!}{b^{l+m+2} a^{k+1}} \left\{ \left[\right. \right.$$

$$\left. \frac{(l+2)(l+1)}{b^2} - \frac{(k+2)(k+1)}{a^2} \right] \left[\sum_{p=0}^{l} \frac{(p+m)!}{p!} \right] +$$

$$\left. \frac{(l+m+1)!\,(2l+m+4)}{b^2 l!} \right\}. \tag{A.10}$$

The number of integrals of this type and of the type given by (A.6), (A.7) and (A.8) was quite large, so a program was written for evaluating them on the IBM 709 computor.

Once the integrals were solved, the matrix elements $\Delta_{k\ell}$ were calculated and the Δ matrix constructed. The inverse of this matrix, Δ^{-1}, was obtained using the method of successive partitioning.[26] It was then a rather easy task to determine the matrix elements of $\mathcal{E}_1'$, which are given by the formula

$$(\mathcal{E}_1')_{ij} = E_i^\circ \delta_{ij} + (\varepsilon - E_i^\circ)(\varepsilon - E_j^\circ) \sum_{k,\ell}^{NINT} \langle \varphi_i^\circ | j_k \rangle (\Delta^{-1})_{k\ell} \langle j_\ell | \varphi_j^\circ \rangle . \tag{A.11}$$

The secular equation (4.30) was solved using the subroutine JACFUL, that generates the eigenvalues of a real symmetric matrix by the Jacobi method.[27]

REFERENCES

1. P. O. Löwdin, J. Mol. Spectry. 10, 12 (1963).

2. P. O. Löwdin, Phys. Rev. 139, A357 (1965).

3. P. O. Löwdin, J. Chem. Phys. 43, S175 (1965).

4. P. O. Löwdin, Proceedings of the Madison Symposium on Perturbation Theory, 1965 (J. Wiley and Sons, Inc., New York, to be published).

5. J. H. Choi, "Lower Bounds to Energy Eigenvalues by the Partitioning Technique," Ph.D. Dissertation, Department of Chemistry, University of Florida (1965).

6. P. O. Löwdin, J. Math. Phys. 3, 969 (1962).

7. P. O. Löwdin, Advances in Chemical Physics (Interscience Publishers, Inc., New York, 1959), Vol. II, P. 207.

8. E. A. Hylleraas and B. Undheim, Z. Physik 65, 759 (1930). J. K. L. MacDonald, Phys. Rev. 43, 830 (1933).

9. P. R. Halmos, Introduction to Hilbert Space (Chelsea, New York, 1957).

10. N. Aronszajn, Proceedings of the Oklahoma Symposium on Spectral Theory and Differential Problems, 1959 (unpublished).

11. P. R. Halmos, Finite Dimensional Vector Spaces (D. Van Nostrand, Princeton, 1958).

12. C. E. Reid, J. Chem. Phys. 43, S186 (1965).

13. J. H. Choi and D. W. Smith, J. Chem. Phys., 43, S186 (1965).

14. C. F. Bunge and A. Bunge, J. Chem. Phys., 43, S189 (1965).

15. E. A. Hylleraas, Z. Physik 54, 347 (1929).

16. C. L. Pekeris, Phys. Rev. 115, 1216 (1959).

17. C. L. Pekeris, Phys. Rev. 126, 1470 (1962).

18. C. E. Moore, Atomic Energy Levels, National Bureau of Standards Circular No. 461 (U. S. Government Printing Office, Washington, D. C., 1959), Vol. I.

19. C. L. Pekeris, Phys. Rev. 126, 143 (1962).

20. G. Temple, Proc. Roy. Soc. (London) A119, 276 (1928).

21. S. O. Goscinski, "Upper and Lower Bounds to Eigenvalues by the Partitioning Technique," Ph. D. Dissertation, Department of Chemistry, University of Florida (1966).

22. W. H. Miller, J. Chem. Phys. 42, 4305 (1965).

23. N. W. Bazley and D. W. Fox, Phys. Rev. 120, 144 (1960).

24. L. Wilets and I. J. Cherry, Phys. Rev. 103, 112 (1956).

25. J. G. Gay, "Lower Bounds to the Eigenvalues of Hamiltonians by Intermediate Problems," Ph. D. Dissertation, Department of Physics, University of Florida (1963).

26. R. A. Frazer, W. J. Duncan and A. R. Collar, Elementary Matrices (Cambridge, London, 1938).

27. F. Prosser, "Matrix Diagonalization by Jacobi's Method," QCPE 4 (1963).

BIOGRAPHY

Timothy Michael Wilson was born August 3, 1938 in Columbus, Ohio. He moved to Saint Petersburg, Florida, in 1950. He was graduated from Saint Paul's High School in June, 1956. In June, 1961, he received the degree of Bachelor of Science in Chemistry from the University of Florida. Since that time he has been pursuing work toward the degree of Doctor of Philosophy at the University of Florida. He was awarded the Kopper's Summer Fellowship in July, 1963, and in September, 1965, he received the DuPont Post-graduate Teaching Assistantship award in Chemistry for the academic year 1965-66.

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy

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